THE DIELECTRIC CONSTANTS OF ORGANIC LIQUIDS.

(a) Binary Mixtures

(b) Disubstituted Benzene Derivatives.

by

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Thesis presented for the degree of Ph.D.

May 1926.

Contents.

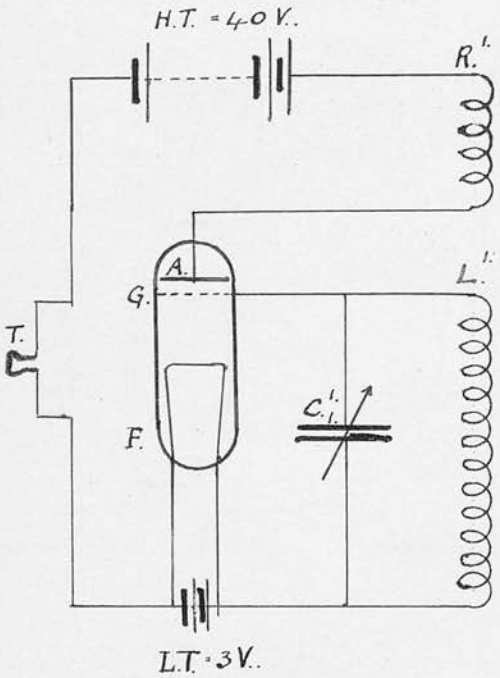
Method of Determination of Dielectric Constant.

That the study of dielectric constants is one which, up till recent years, has received scant attention is largely due to the difficulty which has attended its determination by the old methods of Drude and Nernst. The introduction of the thermionic valve has, however, provided experimenters with a simple source of alternating current and, besides other applications (Wagstaff, Phil.Mag., 1924, 47, 66), it has been employed by several workers in the determination of dielectric constants (Graffunder, Ann.Phys., 1923, 70, 225; Grutzmacher, Z.Physik., 1924, 28, 342; Sayce and Briscoe, J.C.S., 1925, 127, 315). The method to be described now was the result of an endeavour to obtain an apparatus which could be constructed easily from non-expensive materials and which would be simple to use but which, at the same time, would give results of a degree of accuracy sufficient to throw light on some matters of chemical interest.

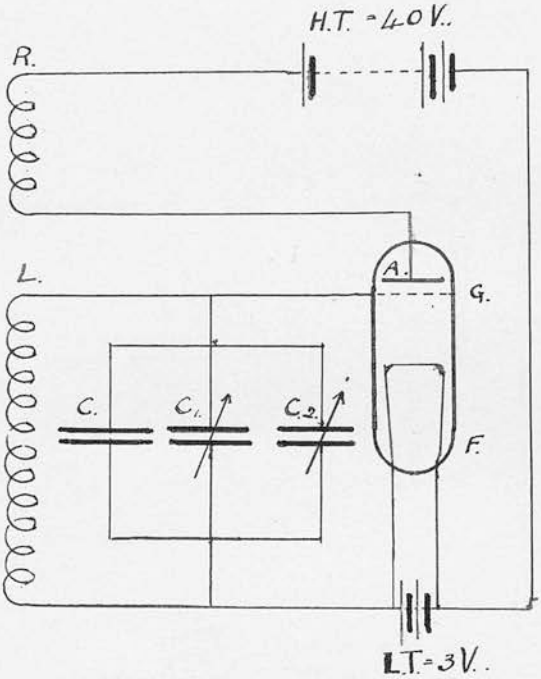
The method used is based on one described by Jackson (Phil.Mag., 1922, 43, 482) and is similar to those used by Grutzmächer (loc.cit.) and by Herweg (Deutsch.Phys.Ges.Ver., 1919, 21, 572). It consists essentially of two simple heterodyne circuits; one of these, termed hereafter for convenience the receiver, is kept constant throughout but the other the emitter, is provided with a variable condenser so that the frequency with which it oscillates may

be/

Fig. 1.



RECEIVER.



EMITTER.

be varied. The emitter is also so constructed that a small condenser, which may be filled either with air or some other substance, can be introduced in parallel with the variable condenser. The receiver will oscillate with a certain frequency determined by its inductance and capacity; so also will the emitter but it may be made to oscillate with the same frequency as the receiver by means of varying the capacity in the circuit. The point of resonance is determined by means of the heterodyne beat note, due to interference between the two circuits, detected by a telephone placed in the receiver circuit. If now the capacity necessary to bring the emitter into resonance be determined first with no condenser in parallel and then with the condenser filled with some substance in parallel, the difference between these two capacities gives the capacity of the condenser filled with that substance. The dielectric constant can then be got by dividing this value by that for the capacity of the condenser filled with air which can be determined in the same way.

The experimental arrangement, by which the above described method was applied, is shown in fig.I.

The Receiver is mounted on an ebonite panel forming the top of a wooden box. The condenser C' is a variable one so that the wave length, at which the determinations are carried out, can be varied if desired.

The/

The Emitter. The components of the emitter are mounted on small pieces of ebonite which are attached to a wooden board, the whole - with the exception of C the experimental condenser, to be described later - being covered with a cardboard dust cover. The variable condensers of this circuit consist of C_1, an air condenser, of capacity .0003 microfarads, of the Dubilier 'Vanicon' type, and in parallel with it, for the purpose of making fine adjustment, a vernier condenser C_2 of the 'Polar' micrometer type, which consists of two co-axial semi-cylinders capable of rotating one within the other. Each condenser is read by means of an elongated pointer of length 6 inches on semicircular scales of a similar radius divided into 180 degrees. In order to remove the effect of body capacity, these condensers are adjusted by means of long ebonite handles of length 3 feet. The inductance and reaction coils used are those supplied by Messrs Burndebt for radio work, the apparatus being so arranged that the coils can be interchanged if other wave lengths are desired.

The method of bringing the emitter into resonance with the receiver consists of setting the large variable condenser by means of a reading telescope to the scale division nearest to resonance and then making the fine adjustment with the vernier condenser. The point of zero sound extends over 10 degrees of the vernier; the two points just where

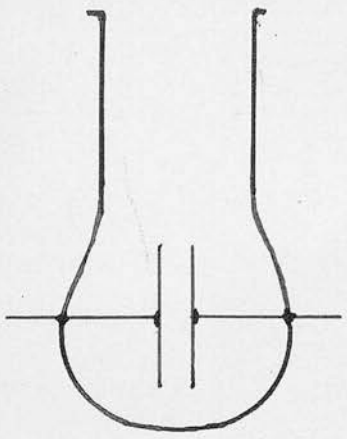
the sound reappears, which are quite sharply marked, are read and the mid point of these two readings is taken as the position of resonance. A source of error occurs through inability to set the large condenser accurately to the scale divisions but this is minimised by repeating each reading ten times and taking the average of the vernier readings so obtained. A typical set of readings consist of

64.6,65.1,64.4,65.6,64.7,64.1,64.7,64.2,64.8,65.0

average 64.7.

The variations are due partly to the reason stated and partly to parallax errors in the telescope readings but the averaging of ten readings was found to give quite reproducible results.

The Experimental Cell. In order to make use of the method as described in the introduction, it is essential to have as little capacity as possible in the cell other than that between the electrodes. Otherwise if say there is a capacity C' of this nature, and C sub. and C air be respectively the capacity between the electrodes with substance and air as dielectric, then the ratio determined is $\frac{C \text{ sub.} + C'}{C \text{ air} + C'}$ which is different from the dielectric constant $\frac{C \text{ sub.}}{C \text{ air}}$. The leads from the electrodes must be such, then, that there is very little capacity between them and this is most easily attained in a cell as shown in fig.2. The electrodes consist of circular gold plates/



(actual size)

FIG 2

plates to which are welded stout platinum wires which are fused through the sides of the glass container. Contact to these leads is made by means of letting them rest on snicks cut in two pieces of brass mounted on ebonite, contact being ensured by the weight of the cell pressing downwards. The cell was closed by a cork carrying a thermometer to note the temperature of the determinations. The cell had capacity approximately .5 micro.micro.farads.

Calibration The apparatus was carefully calibrated in the following manner. The experimental cell containing air was tightly corked and considered as a unit of capacity. The capacity of the cell was then measured at a number of places on the vernier scale and this enabled a calibration curve of the vernier condenser to be drawn in terms of this unit. The large condenser was then calibrated against the vernier and values of the divisions on its scale, also in terms of this unit, were thus obtained. The advantage of this method, it is seen, lies in the fact that the capacity of the condensers is given in terms of/

of the capacity of the experimental cell containing air and accordingly the dielectric constant can be read directly from the capacity, in these units, of the cell containing the given substance. This removes the necessity of requiring to determine the capacity of the cell with air for each substance which saves a considerable amount of time and, also, saves the introduction possibly of quite a large error since a small error in the capacity of the cell with air will cause a much greater error in the dielectric constant, especially if the latter is large. The method, however, requires that no change should take place in the capacity of the cell; in order to prevent any changes due to the expansion of the glass, the cell was not heated when being cleaned but was dried by washing with the usual organic solvents and removal by blowing of air. To guard against any change, the capacity of the cell with air was checked from time to time.

A method of calibration resembling this one has recently been described by Sayce and Briscoe (loc.cit.) but, in place of the experimental cell, they use a small fixed capacity condenser as their unit.

Experimental Difficulties. At first, bright emitter valves - Ediswan C type - were used but it was found that these valves were inclined to heat up causing variations in the frequency of oscillation/

oscillation. By replacement of these by dull emitter valves of the type Osram D.E.3., this difficulty was however largely overcome. In addition, these valves require very little current and, consequently, are not so susceptible to slight changes in the output of the accumulators. To ensure that there were no changes in the frequency of oscillation, the zero point, i.e. the point of resonance without the experimental cell, was taken either before or after each series of readings but, when the apparatus was running well, very little difference was found throughout a short period of ~~the~~ time such as two hours.

One of the main problems which the method presented was the provision of a condenser of wide range which would give reproducible positions in its settings. A condenser with mica dielectric, made by the 'Polar' company, was tried but was not found to be suitable. The 'Vanicon' condenser, however, which is made by Dubilier really for use as a standard for radio work, was found to function satisfactorily. It is now recognized that the use of a large number of small condensers in parallel would be more suitable than a large variable condenser since this would remove the difficulty of setting such a condenser which, as carried out by averaging several readings, proved somewhat laborious and tedious.

Wavelength. The wavelength used was determined by means of a buzzer wave meter. The length was kept/

kept constant throughout the experiments, to be described shortly, at a value of 95 metres, i.e. the frequency was approximately 3×10^6 cycles per second.

Accuracy of Method. Each scale division of C_1 equalled approximately one unit, and 25 scale divisions of the vernier corresponded to a scale division of C_1. The vernier condenser could be read accurately with ease to a quarter of a division and therefore the capacity of C_1 could be read to I/I00th of a scale division. The capacity of the experimental cell could thus be read to a I/I00th of a unit and, as this unit is the capacity of the cell with air, the dielectric constant could be read accurately to .0I. In practice, however, the d.c. could not be repeated with such accuracy due to errors introduced through the difficulty of reading the large condenser as described but, from the figures noted below, it is estimated that the dielectric constant can be obtained by this method with an error not exceeding .02.

Results. By way of testing the apparatus the dielectric constants of some substances with known dielectric constant were determined.

Benzene - The substance used (Kahlbaum für Analyse) was dried over sodium and distilled using a long fractionating column. A constant boiling fraction was obtained. In order to show with what degree of accuracy results are reproducible the figures/

the figures got at room temperature (generally about I5° C.) over a considerable period of time are given.

2.28, 2.28, 2.27, 2.27, 2.29, 2.29, 2.26, 2.28, 2.27, 2.27,

average = 2.28.

After allowance for difference in temperature (temp. coeff. of benzene = .0016 per degree), this value compares favourably with those obtained by Graffunder (loc.cit.) 2.268, t = 25°, and by Grutzmacher (loc.cit.) 2.278, t = 25° both of whom used similar methods and also with that of Isnardi (Z. Physik I922, 9, I53) 2.268. t = 25°, but it is rather higher than those got recently by Sayce and Briscoe (loc.cit.) and by Harris (J.C.S. I925, I27, I065).

Chloroform. The first sample used (B.D.H.) was dried over calcium chloride and distilled using a moderate column. The fraction boiling from 60.5° - 6I° was collected and dielectric constant determined.

k = 5.04, 5.00, 5.0I, t = I5°.

The second sample used was more carefully purified; it was allowed to stand over concentrated sulphuric acid for several days, then washed with water and dried over calcium chloride; on fractional distillation a fraction boiling constant at 6I° was obtained

k = 4.89 t = I4°

= 4.85 t = I6°

The temperature coefficient of chloroform (.0I72 per degree. Ratz. Zeit. fur Phys. Chem., I9, I06.) is quite considerable and, on making correction for temperature/

temperature, these figures are in good agreement with one another. The values quoted in the literature vary considerably which is probably due to the change in the value noted here on further purification; the most recent value is that given by Harris (loc.cit.), who however used a different method, $k = 4.64I7$, $t = 25^{\circ}$. This gives a slightly lower value than the one recorded here but other experimenters obtain higher results, $k = 4.760$, $t = 25^{\circ}$, (Isnardi, loc.cit.), 4.8II. $t = 25^{\circ}$.(Tangl, Ann. Phys. I903, IO, 748), and 4.962 $t = 25^{\circ}$.(Grützmächer loc.cit.)

Ethyl Ether. The sample used was washed several times with small quantities of water, dried over calcium chloride, filtered and then dried over sodium wire. It was fractionated three times over phosphorous pentoxide and fraction boiling over half a degree was used (B.P. $34.5^{\circ} - 35^{\circ}$)

$k = 4.50$ $t = II^{\circ}$

$= 4.44$ $t = I4^{\circ}$

These values compare very favourably with those given in the literature. (temp.coeff. = .0I86 per degree, Ratz loc.cit.)

$k = 4.37$ $t = I8^{\circ}$ Turner (Zeit. für Phys. Chem. I900, 35, 385)

$k = 4.35$ $t = I8^{\circ}$ Coolidge (Wied. Ann. I899, 69, I25.)

From these figures, then, it is seen that, setting out from material, which can be readily obtained for radio work, an apparatus has been constructed capable of giving, quite rapidly, values for the dielectric constant with a degree of accuracy which, though/

though not sufficient to investigate some of the important physical aspects of the subject, suffices for the investigations of more chemical interest to be described now.

The Dielectric Constants of Binary Liquid Mixtures.

In the past much work has been done to endeavour to find a simple formula able to give the physical properties of a binary liquid mixture from those of its components. Most attention has been given, in this direction, to surface tension and viscosity but with neither has any success been achieved. In particular, viscosity has been very closely studied first by Dunstan (J.Chem.Soc., 1904, 85, 817 et seq.) and latterly by Kendall (J.Amer.Chem.Soc. 1917, 39, 1787 et seq.); the latter studied mixtures which from other data could be regarded as nearly ideal but found that, even with these mixtures, no formula agreed with the experimental results. Very little work, however, has been done on the dielectric constants of such liquid mixtures which is surprising as more success is probable with the dielectric constant, a static property, than with either of the properties mentioned, which are both essentially kinetic. This lack of experimental knowledge is probably due to the difficulty, already mentioned, in the determination of dielectric constant rather than any to disregard of the importance of such data. An apparatus, as described, however allows of a simple determination of this property and, by means of it, an investigation of the dielectric constants of liquid/

liquid mixtures has been carried out with very interesting results.

The dielectric constant of a substance is defined as the ratio of the capacity of a condenser filled with that substance to that of the same condenser containing a vacuum. Thus, by this definition it is a property of a certain volume of substance, and when two dielectric constants are compared, the properties of the numbers of molecules of the two substances contained in equal volumes are compared. It follows then, when certain volumes of two liquids are mixed, that if (I) the dielectric properties of the two kinds of molecules remain the same as before mixing and if (2) the respective molecules retain the same volume in the mixture as in the pure states (i.e. the total space is not shared equally amongst the different kinds of molecules), then the dielectric constant of the mixture should be obtained by adding together the volume percentage fractions of the dielectric constants of the two components, i.e. the rule obeyed should be the one put forward by Silberstein (Wied. Ann. I895, 56, 66I),

$$k = \frac{k_1 V_1 + k_2 V_2}{V_1 + V_2}$$

where k, k_1, and k_2 are the dielectric constants of the mixture and the two components and V_1 and V_2 are the volumes present of the two components.

This formula does not allow of any change

of/

of volume on mixing but for mixtures, in which the change is slight, this rule should be obeyed approximately. Large volume changes generally are due to changes such as association taking place and these will influence the dielectric properties of the molecules; in what way this occurs can only be found by observing experimentally the nature of the deviation from Silberstein's Law.

Silberstein (loc.cit.) found that this formula held for a mixture of benzene and phenyl acetate. Linebarger (Zeit.Phys.Chem.,I896,20,I3I). Drude (ibid, I897,23,30I) and Philip (ibid,I897,24,I8) all failed to find agreement with this formula which led Philip to suggest another;

$$\frac{\sqrt{k}-I}{d}\ I00 = \frac{\sqrt{k_1}-I}{d_1}\ p_1 + \frac{\sqrt{k_2}-I}{d_2}\ (I00 - p_1)$$

where k, ~~and~~ k_1, and k_2 are as before, p_1 is the percentage composition by weight of one component and d, d_1, d_2 are the densities respectively of the mixture and the two components. He,however,only quotes two mixtures, benzene - ether and chloroform - carbon disulphide which give close agreement. Dobroserdoff (J.Russ.Phys.Chem.Soc.I9I2,44,679) investigated a large number of mixtures obtained from non associated organic liquids; he classified his results according to the curves of dielectric constant against percentage composition and obtained three groups (a) straight line curves (b) curves concave and (c) curves convex to axis of concentration. None of the mixtures

obeyed/

obeyed Philips formula but those of group (a) followed Silberstein's volumetric mixture rule approximately. The deviations of groups (b) and (c) from the straight line were explained as due to the formation of chemical compounds; as one of the components of many of these mixtures was such an inert substance as benzene, heptane or carbon tetrachloride this explanation, however, hardly seems very feasible and with a view to further testing it, an investigation was started with mixtures, one component of which was benzene and the other a benzene derivative, which would not be expected to enter into chemical combination. The results obtained are given in the next paragraph.

Experimental Part.

The results obtained are tabulated in the following pages. In general, four different concentrations were taken for each mixture; the mixtures were made up by means of pipetting the required volumes and these were checked by weight with the exception of the first few mixtures which were investigated. In columns I and 2, the percentage compositions by volume and weight of the component other than benzene are given; in column 3, the dielectric constant (k) found experimentally, in column 4, k calculated from the volumetric mixture formula, and in column 5, the difference between k calc. and k obs. are given.

The mixture/

The mixtures of each series were done in sequence and the temperature did not vary from that noted by more than half a degree throughout the series. The liquids used were mostly Kahlbaum reagents but in a few cases they were B.D.H., and in some others they were prepared in the laboratory by the usual methods. In all cases, they were dried over suitable reagents and fractionally distilled until a constant boiling fraction was got, in some cases several fractionations were necessary before a fraction boiling constant over ·2° was obtained.

The curves of dielectric constant against % composition by volume for these mixtures are drawn in figs. 3 – 7.

Table I/

FIG. 3.

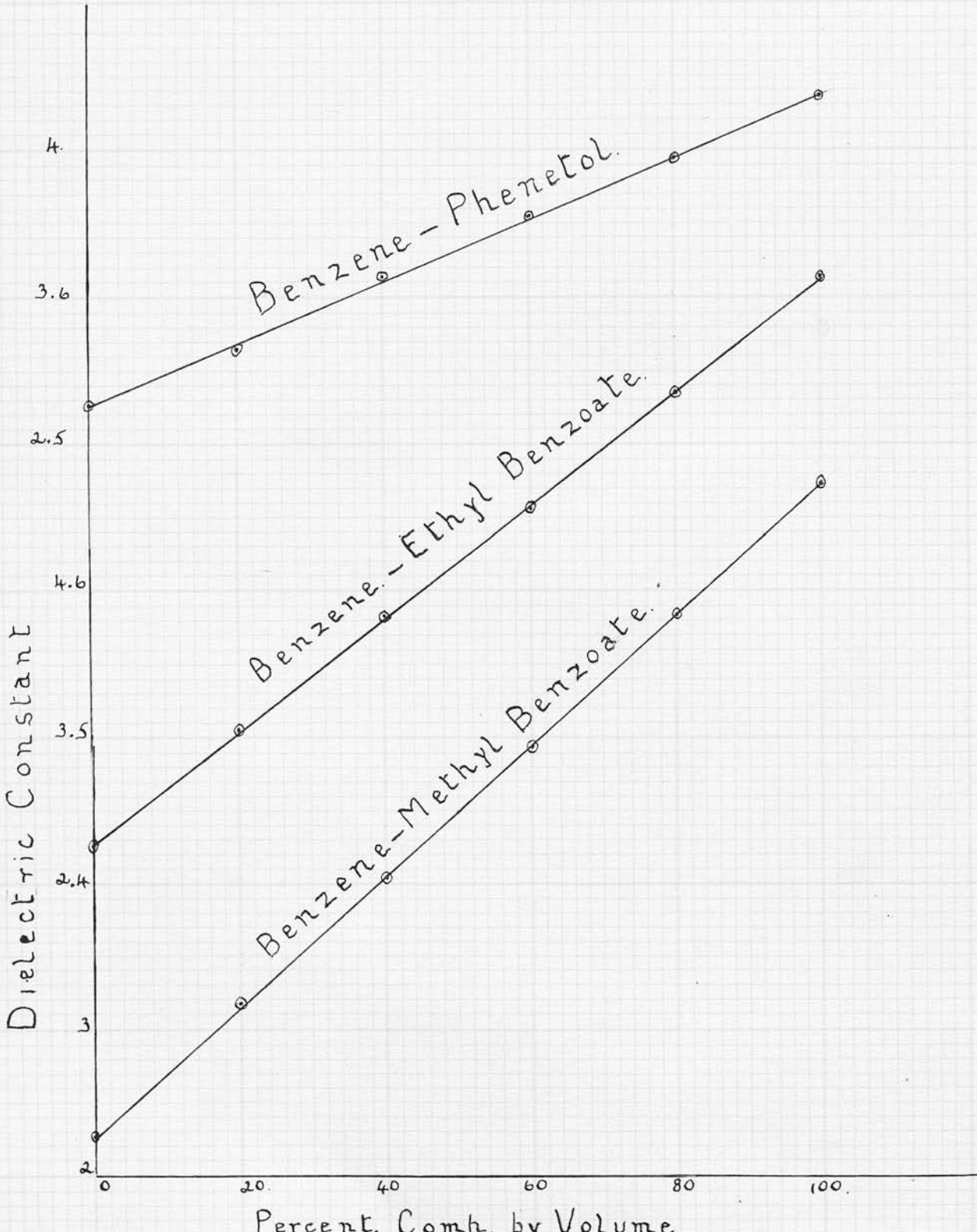

Benzene - Phenetol.
Benzene - Ethyl Benzoate.
Benzene - Methyl Benzoate.
Dielectric Constant
4.
3.6
2.5
4.6
3.5
2.4
3
2
0
20.
40
60
80
100.
Percent. Comp. by Volume.

Table I. Benzene and Methyl Benzoate Temp. = I2° C.

Comp. by Vol.	k. obs.	k. calc.	k. obs. -k. calc.
0	2.28	2.28	
20	3.I8	3.I7	+.0I
40	4.04	4.06	-.02
60	4.93	4.94	-.0I
80	5.82	5.83	-.0I
I00	6.72	6.72	

Table 2. Benzene and Ethyl Benzoate. Temp. = I5° C

Comp. by Vol.	Comp. by weight	k. obs.	k. calc.	k. obs. -k. calc.
0	0	2.27	2.27	
20	22.9	3.09	3.04	+.05
40	44.3	3.85	3.8I	+.04
60	64.2	4.59	4.58	+.0I
80	82.8	5.32	5.35	-.03
I00	I00	6.I2	6.I2	

Table 3. Benzene and Phenetol Temp. = I5° C.

Comp. by volume	Comp. by weight	k. obs.	k. calc.	k. obs. -k. calc.
0.	0	2.28	2.28	
20	2I.5	2.63	2.68	-.05
40	42.3	3.I2	3.II	+.0I
60	62.I	3.53	3.54	-.0I
80	8I.5	3.95	3.95	.00
I00	I00	4.37	4.37	

FIG. 4.

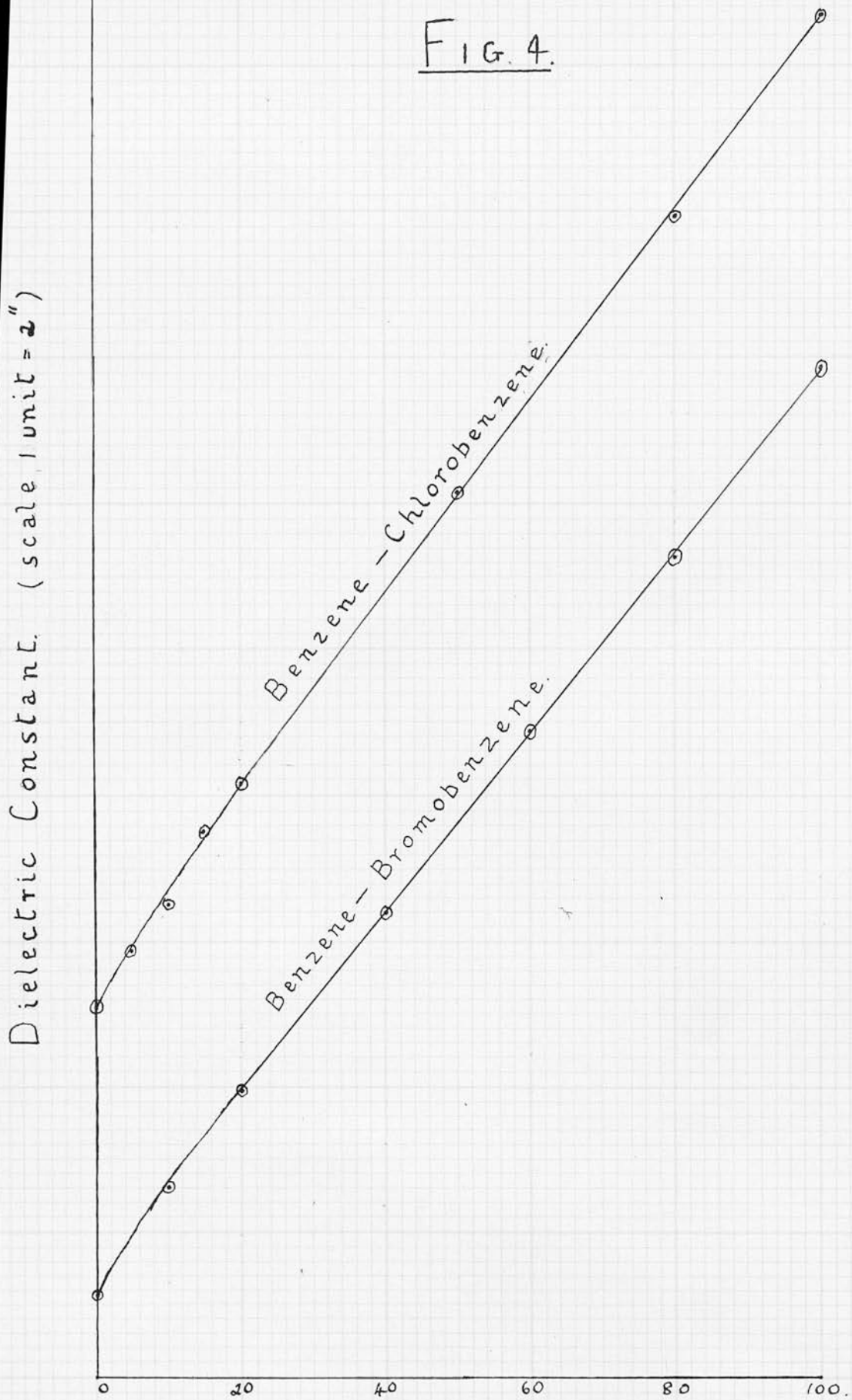

Dielectric Constant. (scale 1 unit = 2")
Benzene - Chlorobenzene.
Benzene - Bromobenzene.
0
20
40
60
80
100.
Percent. Comp. by Volume.

Table 4. Benzene and Bromobenzene Temp. = I6°

Comp. by volume	k. obs.	k. calc.	k. obs. -k. calc.
0	2.28		
I0	2.65	2.60	+.05
20	2.99	2.92	+.07
40	3.60	3.55	+.05
60	4.2I	4.I9	+.02
80	4.8I	4.82	-.0I
I00	5.46		

Table 5. Benzene and Chlorobenzene. Temp. = I5°

Comp. by volume	Comp. by weight	k. obs.	k. calc.	k. obs. -k. calc.
0	0	2.27		
5	6.23	2.47	2.44	+.03
I0	I2.2	2.62	2.6I	+.0I
I5	I8.3	2.88	2.78	+.I0
20	23.7	3.04	2.95	+.09
50	55.8	4.04	3.97	+.07
80	83.5	4.99	4.99	.00
I00	I00	5.67		

FIG. 5.

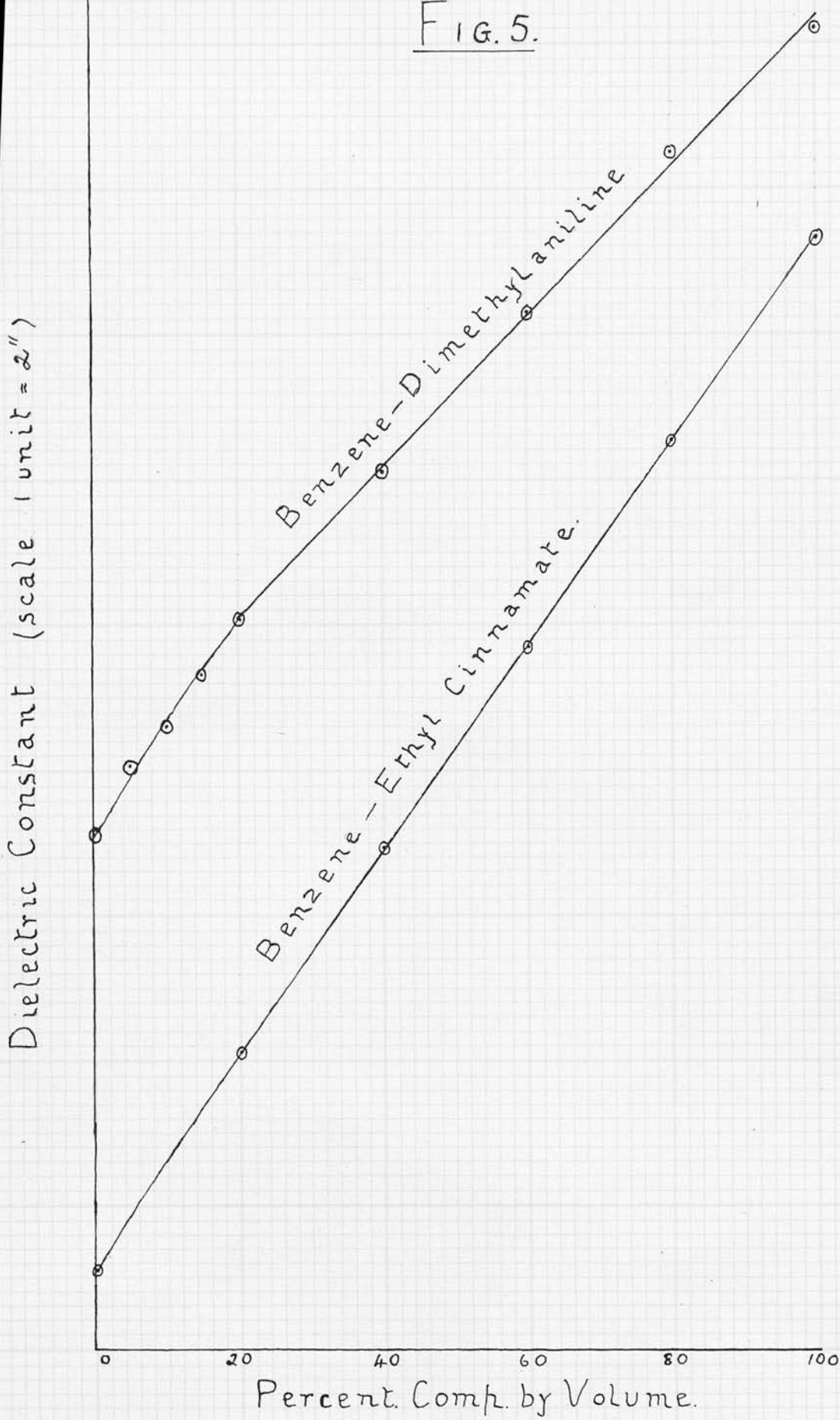

Dielectric Constant (scale 1 unit = 2")
Benzene-Dimethylaniline
Benzene-Ethyl Cinnamate.
0
20
40
60
80
100
Percent. Comp. by Volume.

Table 6. Benzene and Dimethylaniline Temp = I4°

Comp. by volume	Comp. by weight	k. obs.	k. calc.	k. obs. -k. calc.
0	0	2.28		
5	5.34	2.5I	2.42	+.09
I0	I0.7	2.65	2.56	+.09
I5	I6.I	2.83	2.69	+.I4
20	2I.2	3.02	2.83	+.I9
40	42.0	3.52	3.39	+.I3
60	62.0	4.07	3.94	+.I3
80	8I.4	4.63	4.50	+.I3
I00	I00	5.05		

Table 7. Benzene and Etnyl Cinnamate. Temp = I6°

Comp. by volume	Comp. by weight	k. obs.	k. calc.	k. obs. -k. calc.
0	0	2.27		
20	22.8	3.03	2.98	+.05
40	44.I	3.74	3.69	+.05
60	63.9	4.42	4.40	+.02
80	82.5	5.I4	5.I2	+.02
I00	I00	5.83		

FIG. 6.

Dielectric Constant.
Scale
aniline 1 unit = 1"
nitrobenzene 5 units = 1"
benzaldehyde 2 units = 1"
Benzene-Benzaldehyde
Benzene-Nitrobenzene
Benzene-Aniline
35.03.
7.20.
0
20
40
60
80
100
Percent. Comp by Volume.

Table 8. Benzene and Aniline Temp. = I3.5°

Comp.by volume	k.obs.	k.calc.	k.obs. -k.calc.
0	2.28		
20	3.I6	3.27	-.II
40	4.05	4.26	-.2I
60	5. 02	5.26	-.24
80	6.07	6.26	-.I9
I00	7.20		

Table 9. Benzene and Benzaldehyde Temp. = I4.5°

Comp.by volume	Comp.by weight	k.obs.	k.calc.	k.obs. -k.calc.
0	0	2.27		
20	23.0	4.8I	5.44	-.63
40	44.4	7.46	8.59	-I.I3
60	64.3	I0.57	II.85	-I.28
80	82.5	I3,92	I4.9I	- .99
I00	I00	I8.07		

Table I0. Benzene and Nitrobenzene Temp. = I4.5°

Comp.by volume	Comp.by weight	k.obs.	k.calc.	k.obs. -k.calc.
0	0	2.28		
20	25.5	6.74	9.23	-2.49
40	47.6	II.90	I5.38	-3.48
60	67.2	I8.I9	2I.93	-3.74
80	84.3	25.8I	28.48	-2.67
I00	I00	35.03		

FIG. 7.

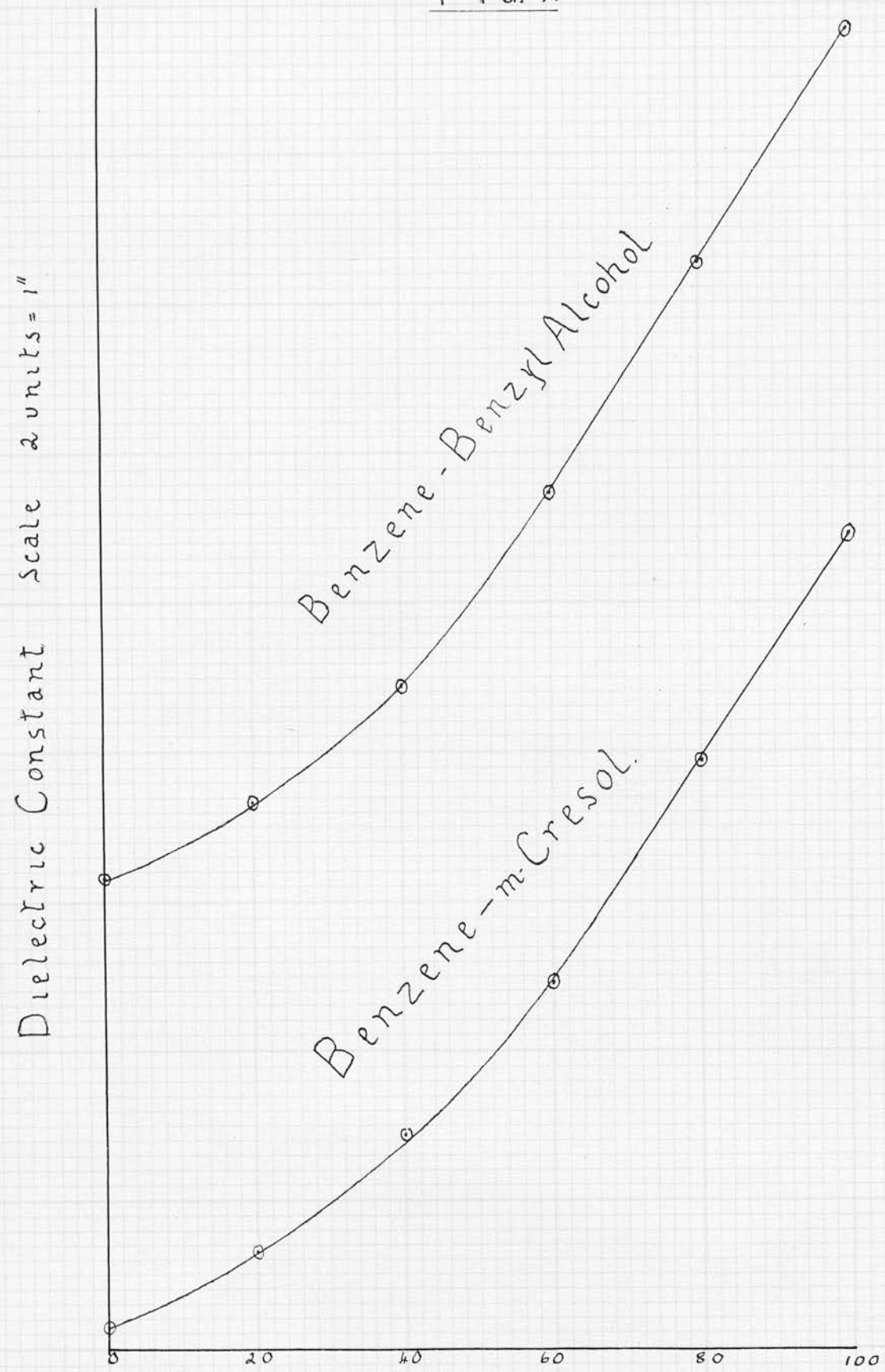

Dielectric Constant Scale 2 units = 1"
Benzene-Benzyl Alcohol
Benzene-m-Cresol.
0
20
40
60
80
100
Percent. Comp. by Volume

Table II. Benzene and Benzyl Alcohol. Temp. = 14°

Comp.by volume	Comp.by weight	k.obs.	k.calc.	k.obs. -kcalc.
0	0	2.28		
20	21.4	3.37	4.55	-1.18
40	44.3	4.96	6,82	-1.86
60	63.6	7.46	9.09	-1.63
80	82.3	10.58	11.36	- .78
100	100	13.63	13.63	

Table 12. Benzene and m.Cresol. Temp. = 16°

Comp.by volume	Comp.by weight	k.obs.	k.calc.	k.obs. -k.calc.
0	0	2.28		
20	22.5	3.28	4.41	-1.13
40	43.6	4.82	6.55	-1.73
60	63.5	6.95	8.68	-1.73
80	82.3	9.86	10.82	- .96
100	100	12.95		

Discussion of Results.

Examination of the curves drawn in figs.3 – 7 shows that the mixtures may be divided into two main classes:-

(I) the mixtures given in figs 3,4, and 5,which either give straight lines or deviate only slightly from such.

(2) the mixtures given in figs 6 and 7, whose curves deviate considerably from straight lines giving markedly lower values of the d.c. than is required by the volume rule.

The first class may further be divided into two sub-classes:-

I(a) the mixtures which give straight lines (fig.3) and obey Silbersteins rule accurately.

I(b) the mixtures which deviate slightly from straight lines giving values higher than the calculated, the deviations being greatest at small concentration of the component other than benzene. (figs.4 and 5.)

The actual classification may be here summarised.

Class I. (a) Mixtures of benzene with methyl benzoate, ethyl benzoate and phenetol.

(b) Mixtures of benzene with bromo-benzene,chlorobenzene,dimethyl-aniline and ethyl cinnamate.

Class 2. Mixtures of benzene with aniline, benzaldehyde/

benzaldehyde, nitrobenzene, benzyl alcohol and m-cresol.

In as much as a number of mixtures are found to obey Silberstein's rule accurately and some others only to deviate slightly from it, it would appear, at first sight, that this rule is the correct one for an ideal solution and variations from it are due to changes taking place on mixing. If such is the case, it is necessary to explain the large deviations of mixtures of the second class; oncursory examination one sees at once that, whereas the mixtures of class I are those of substances with benzene which give approximately normal molar weights in benzene, the substances mixed with benzene in class 2. mixtures are known to give abnormally high molar weights in benzene due to association (see Turner's 'Molecular Association, appendix). This suggests that the deviations from the volume rule of the mixtures of the second group are due to changes in the degree of association of the second component when mixed with benzene.

In order to obtain definite proof that such changes in association are taking place, accurate molecular weight determinations of the substances mixed with benzene were carried out by means of the usual depression of the freezing point method. Care was taken to have the conditions the same throughout all /

Table 13.

Molecular Weight Determinations. - Solvent Benzene.

Substance	Theor. M.W.	Present results Conc. gms/100 gms.	M.W.	Other Investigators Conc.	M.W.	Investigator	Percent Dev. M.W.det.- M.W.theor.
First Group							
Methyl Benzoate	136	2.76	130				-4.5
		4.26	131				
Ethyl Benzoate	150	2.68	143	3.41	144	Beckmann	- 5
		4.01	144.5	9.51	146	do	
Phenetol	122	2.50	116	2.59	119	do	- 5
		3.75	117	7.25	121	do	
Bromobenzene	157	2.84	146	1.50	154	Turner	- 7
		4.22	149	6.63	157	do	
Chlorobenzene	113	1.93	105	1.75	111	do	
		2.86	107.5	7.55	114	do	- 5
Dimethylaniline	121	2.26	113				- 7
		3.17	115				
Ethyl Cinnamate	176	3.30	166				
		4.45	168				- 6
Second Group							
Aniline	93	1.92	105	1.83	104.5	Turner	+ 12
		2.81	109	3.54	110.6	do	
Benzyl Alcohol	108	2.58	130	2.78	132	Anwers	+ 20
		4.22	155	5.03	165	do	
m.Cresol	108	2.68	124				+15
		4.01	131				
Nitrobenzene	123	2.39	121				- 2
		3.62	124	3.65	124	Beckmann	
Benzaldehyde	106	2.47	103.5	2.09	103	Beckmann	- 2
		3.34	105	6.88	108	do	

all the determinations thus ensuring truly relative values. The depression taken was approximately the same in all cases and was a large one (one degree) in order to minimise the error due to reading the thermometer; a second value was taken, at slightly greater concentrations, as a check of the first value and from these it is estimated that the results are accurate to one unit. The values obtained are given in table I3 along with the results of ~~the~~ other investigators; the present values are found to be in satisfactory agreement with the latter.

The values for the substances of class I are all from 5 - 7% below the normal, but as ethyl and methyl benzoate are both generally considered to give very nearly examples of ~~an~~ ideal solutions when mixed with benzene there is probably an inherent error of this extent in the method. If a divergence of this amount be considered that of a non associating substance, it is seen from this table that the substances of the second class give values which are greater than this normal value; aniline, benzyl alcohol and m-cresol all give very high results but nitrobenzene and benz~~a~~aldehyde both give figures only 3% greater relatively than the substances of the first class. The concentrations at which these determinations are carried out (3%), however, are much smaller than the most dilute solutions (generally 20%) of which the dielectric constant has been examined/

examined and from the work of other investigators it is found that the molar weight of both these substances increases with concentration much more rapidly than do substances of the first class. This may be verified from table I4 which are results obtained by Beckmann (Zeit.fur Phys.Chem.,2,717); the figures for ethyl benzoate and phenetol are included for comparison.

Table I4.

Molecular Weight Determinations in Benzene.

Nitrobenzene in Benzene (normal value I23)					
conc.(gms./I00gms benzene)	.89	3.64	6.69	I0.84	I8.I8
Δ (depression)	.37	I.44	2.55	3.94	6.22
mol. weight	II9	I24	I28	I35	I43.
Benzaldehyde in Benzene (normal value I06)					
conc.	.5I	2.09	6.88	I2.I8	I7.64
Δ	.24	I.00	3.I3	5.24	7.59
mol. wt.	I02	I03	I08	II4	II4.
Phenetol in Benzene (normal value I22)					
conc.	.65	2.59	7.25	I0.85	I6.55
Δ	.26	I.06	2.95	4.34	6.46
mol. wt.	I20	II9	I2I	I22	I25
Ethyl Benzoate in Benzene (normal value I50)					
conc.	.4I	3.43	9.5I	I5.30	
Δ	.I4	I.I6	3.I9	5.02	
mol. wt.	I42	I44	I46	I49	

These figures show conclusively that the second components of class 2 mixtures (i.e. the component other than benzene) all give molecular weights in benzene solution greater than normal, indicating that association takes place with these substances. Further proof of this may be got from the changes of volume on mixing. Such changes were determined for some of the mixtures by means of density determinations of which the results are given in table I5. The mixtures were so chosen that the two components were present, in each case, in approximately equimolecular proportions; the pyknometer, by which the density was determined, was immersed in a water bath at room temperature which maintained the temperature constant to within half a degree.

Table I5.

Determination of change of Volume on Mixing.

Mixture	Conc. gms. benzene per 100 gms. soln	D_4^{15}	D_4^{15} (theor)	Ddet. - D theor.
Group I.				
Benzene - methyl benzoate	40.70	I.0II0	I.0I09	+.000I
Benzene - ethyl benzoate	30.I3	I.002	I.00I6	+.0004
Benzene - phenetol	54.3I	.9234	.9238	-.0004
Benzene - bromobenzene	44.50	I.228	I.2273	-.0007
Benzene - chlorobenzene	45,95	I.0074	I.0078	-.0004
Benzene - dimethylaniline	40.39	.9292	.9294	-.0002
Group 2.				
Benzene - aniline	5I.36	.9564	.9536	+.0028
Benzene - benzyl alcohol	45.86	.9792	.9773	+.00I9
Benzene - m.cresol	45.2I	.9698	.9686	+.00I2
Benzene - nitrobenzene	46.04	I.0605	I.0597	+.0008

From/

From these figures one sees that, within the error due to temperature changes of half a degree, the mixtures of class I show no appreciable change of volume on mixing whereas those of the second class all have greater densities than the theoretical. This contraction on mixing is very probably due to the association which the previous figures have shown to be taking place in these mixtures.

These results, then, show that no appreciable association is taking place in the mixtures of the first class but quite marked changes in the degree of association occur with those of the second class. If such association be considered as taking place in a manner represented in fig.8. it follows that its effect will be to cause a partial neutralisation of some of the dipoles, and accordingly bring about a lowering of the dielectric constant. The abnormally low values of the dielectric constants of the mixtures of the second class can thus be explained as due to association of the component of the mixture other than benzene.

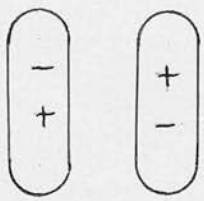
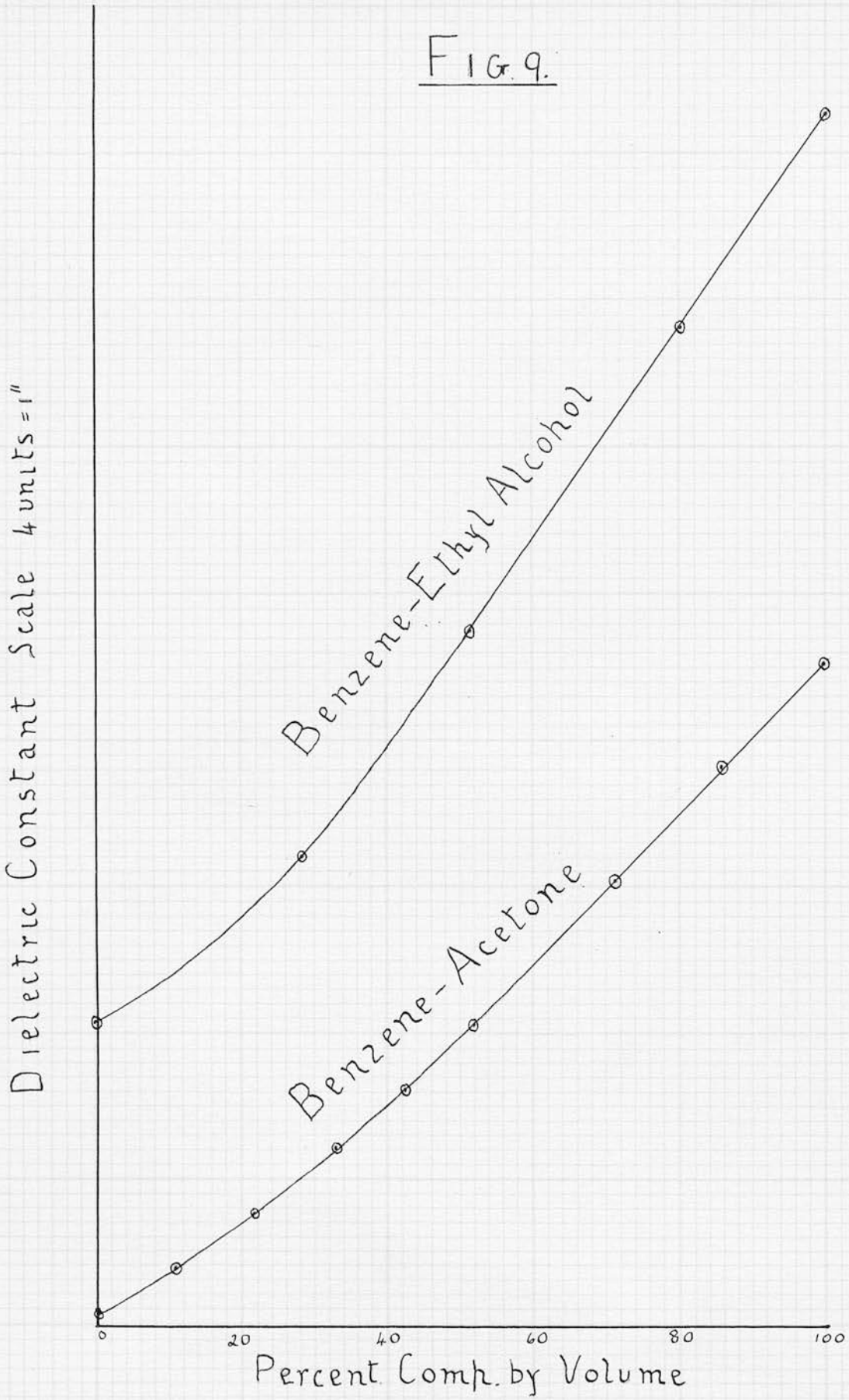


fig 8.

A difference is noted between the curves of the second class given in fig.6. and those given in fig.7. The former are quite regularly curved throughout/

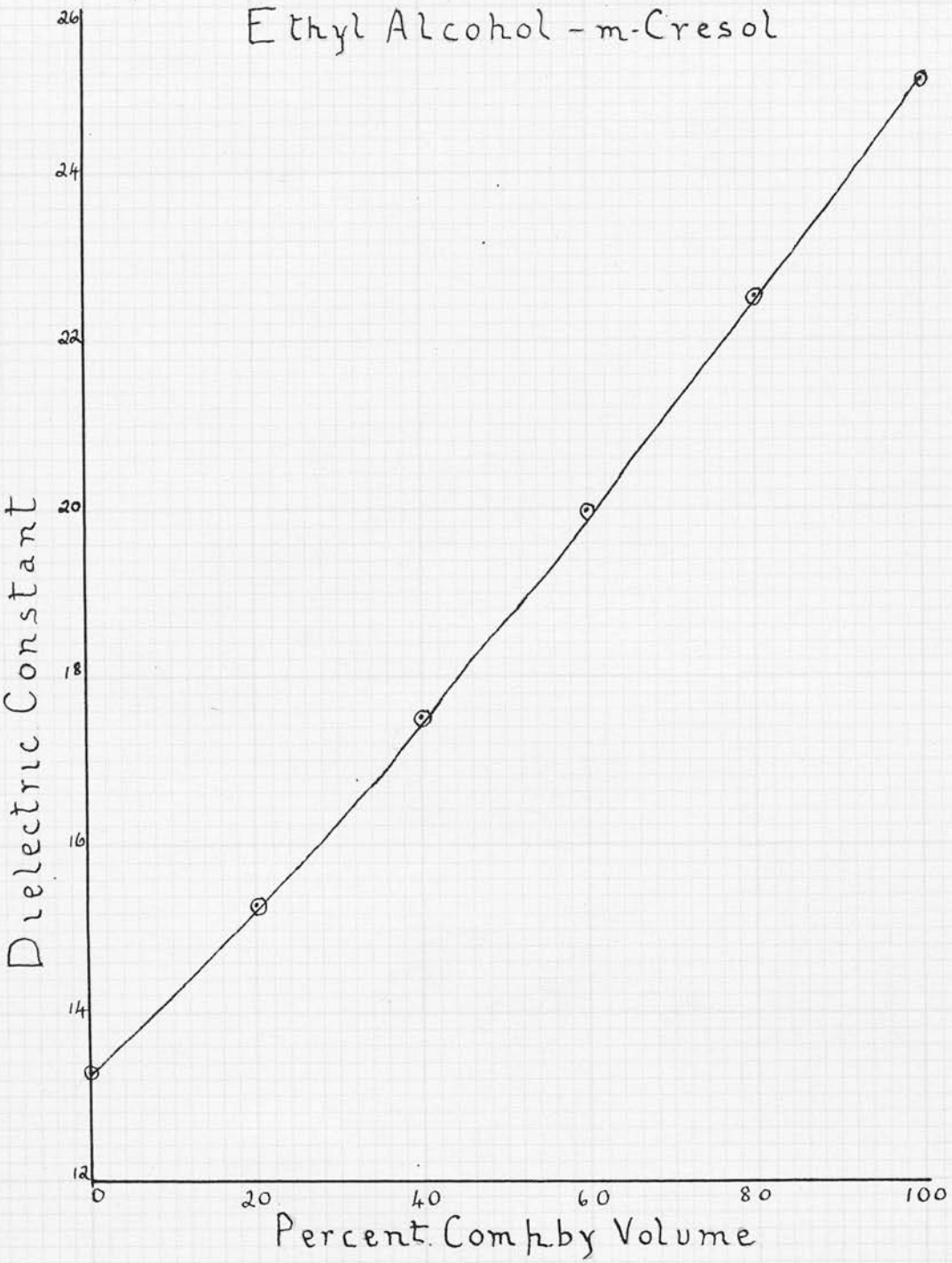
FIG. 9.


Dielectric Constant Scale 4 units = 1"
Benzene-Ethyl Alcohol
Benzene-Acetone
0
20
40
60
80
100
Percent Comp. by Volume

throughout the entire range of concentration but the latter, although curved in the same way for half the range, break away from this regularity at about 50% concentration and then merge into linear curves. This is interesting for there is a difference between the second components of the two sets of mixtures; aniline, nitrobenzene and benzaldehyde are all substances unassociated in the pure state, (association factor by Ramsay and Shields method, I.02, .97 and .93 respectively) but benzyl alcohol and cresol are both hydroxylic substances which are generally regarded as associated in the pure state. This type of curve seems to be typical of such associated substances for similar curves are got for mixtures of benzene - ethyl alcohol (Philip, loc.cit.) and benzene - acetone (Drude loc.cit.) as may be seen from fig.9. where the curves got by these investigators are reproduced. The explanation of such curves appears to lie in the fact that the substance is associated in the pure state. The dielectric constant will reach a maximum deviation when the association is at its greatest; in the mixtures of fig. 6., this occurs at 50% concentration and at greater concentrations the association falls away until it is normal at 100%; in the mixtures of fig.7., however, the association appears to reach a maximum and then fall away until it has a value similar to what it is in the pure state; from that point on, the dielectric constant follows a linear curve.

Before/

FIG. 10.


Ethyl Alcohol - m-Cresol
Dielectric Constant
26
24
22
20
18
16
14
12
0
20
40
60
80
100
Percent Comp. by Volume

Before leaving these considerations of association, another mixture is worthy of recording here. It is well known that, although the molar weights of hydroxylic substances such as phenol are abnormal in inert solvents, they are practically normal in other hydroxylic substances. As cresol mixed with benzene gives a curve which deviates strongly from that which is being suggested as the ideal mixture curve, and as such deviation is being explained as due to association of the cresol in the inert solvent, it is interesting to note the dielectric constant curve of cresol in a hydroxylic solvent in which its molar weight will probably be normal. The results got for a mixture of cresol-ethyl alcohol are given in table I6 and the curve is drawn in fig. I0

Table I6.

Ethyl alcohol and m-cresol Temp. = I3°

%Comp. of alcohol by wt.	by vol.	D.C.(k). observed	k calc.from volume rule	k.obs. - k.calc.
0	0	I3.36		
I6.I9	20	I5.30	I5.70	-.40
33.88	40	I7.57	I8.I5	-.58
53.6I	60	20.0I	20.40	-.39
75.55	80	22.54	22.75	-.2I
I00	I00	25.I0		

In comparison with the cresol - benzene figures, the dielectric constants for this mixture only differ slightly from those required by the volume rule and, as much smaller changes of association take/

take place in such mixtures as cresol-alcohol, this result supports in a general way the view that the deviations of the second class mixtures are due to association. Too much reliance however cannot be placed on this result for, in such a mixture, not only may changes of the degree of association of cresol take place, but also similar changes with alcohol may occur and in addition there is the possibility of association products being formed between alcohol and cresol. That the dielectric constant curve is practically normal shows that these various effects counterbalance one another.

Consideration of Mixtures of the First Group.

Up till now, we have been concerned with changes on mixing more or less of a chemical nature. There may, however, be changes of another kind. Any molecule in the liquid state is subject to various repulsive and attractive forces as well as to collisions from neighbouring molecules; in order to designate the sum total of these effects, Washburn has introduced the term 'thermodynamical environment' and it is obvious that this environment will exert an influence on how the molecules behave. A solution will only be ideal, if this environment is the same in the solution as in both pure liquids; this, however, is a limiting case and in general the environments of the molecular species in any two liquids are different. Accordingly/

Accordingly a molecule of any liquid will be exposed to different forces in a mixture with a liquid of different 'thermodynamical environment' than it is in the pure state. Such differences will in general have/an effect on the physical properties of the respective molecules and we may enquire what effect will be produced by them on dielectric constants.

According to the well known work of Debye (Phys.Zeit.1912,13,97; Verh.d.Deut.Phys.Ges.1913, 15,777), a molecule possesses a permanent dipole and thus when a liquid is subjected to an alternating electric field, as in the case when the dielectric constant is determined, the molecules may be thought of as maintained in a state of rapid vibration. The amount of this vibration, however, will be an equilibrium condition depending (1) on the strength of the external field (2) on the size of the dipoles (3) on the heat motions of the molecules and (4) on the cohesive forces, just referred to, acting on any molecule by its neighbours. The first three conditions are constant in the pure and mixed states but the fourth condition, as we have seen, may vary; if the cohesive forces acting in/a liquid A are smaller than those acting in a liquid B, then, when A and B are mixed, the forces acting on B will be less in the mixture than in B itself and, consequently, the B molecules will have greater freedom of vibration causing an increase of their dielectric properties. On the other/

other hand if the cohesive forces in A are greater than those in B then the vibrations of the B molecules will be damped causing a diminution of their dielectric properties. Such effects will of course be greatest in dilute solutions and it is interesting to note that, in the case of mixtures of class I (b), the dielectric constants found are slightly greater than those required by the volume rule and that the deviations are greatest at small concentrations. It now falls to be seen if proof is available as to whether any difference in the cohesive forces exist in these liquids which could account for these slight rises.

Definite proof of such a question, at the present extent of knowledge about the liquid state, is difficult to obtain but some indications of such differences may be got from the work of Hildebrand who, in a recent series of papers on solubility (J. Am. Chem. Soc., 1916, 38, 1458 et seq.), has shown the importance of such cohesive forces in the prediction of solubility. He has introduced the term 'internal pressure' to serve as an indication of the cohesive forces acting in liquids and has calculated its values from various data such as surface tension, critical data, heat of vaporization and coefficient of expansion. From the figures obtained, he shows that non polar liquids with approximately equal internal pressures obey Raoult's Law satisfactorily when mixed but differences in internal pressures cause deviations from/

from the latter. This law, moreover, is now accepted as one of the best criteria of an ideal solution and, accordingly, one may conclude that non-polar liquids with approximately equal internal pressures, as calculated by Hildebrand, form very nearly ideal solutions. Such a result, obtained on experimental grounds, shows that these internal pressures give a fair indication of the cohesive forces exerted on any molecule in the liquid state. It was, therefore, thought to be of interest to calculate the internal pressures for the liquids of class I and these are given in Tables I7 and I8; the figures necessary for the calculations were obtained from the tables of Landolt and Bornstein.

Table I7.

Internal Pressures from Surface Tension.

($\pi = \frac{\alpha}{V^{\frac{1}{3}}}$ where α and V are surface tension and molecular volume respectively).

Benzene	6.54	Chlorobenzene	7.05
Ethyl Benzoate	6.6I	Bromobenzene	7.5
Methyl Benzoate	7.44	Dimethylaniline	7.28
Phenetol	6.46	Ethyl Cinnamate	6.73

Table I8.

Internal Pressures from Critical Constant Data.

($\pi = \frac{\alpha}{V^2} \times 10^5$).

Benzene	4.49	Bromobenzene	5.I6
Phenetol	4.37	Chlorobenzene	4.88
		Dimethylaniline	4.64

Owing to ~~the~~ lack of critical constant data table I8 is incomplete but from table I7 we see that both/

both ethyl benzoate and phenetol have internal pressures very close to that of benzene and, as the molar weight in benzene of both liquids is normal and neither show an appreciable change of volume on mixing, the mixtures of both these liquids with benzene appear to be close approximations to ideal solutions. The value of the internal pressure of methyl benzoate is peculiar, however, being much higher than that of ethyl benzoate which leads to the unlikely result that, while ethyl benzoate - benzene should give practically an ideal solution, methyl benzoate - benzene should not; it would appear probable that this discrepancy with methyl benzoate is due to experimental errors in the determination of the surface tension, especially as the dielectric behaviour of benzene - methyl benzoate is the same as that of benzene - ethyl benzoate , and that the former mixture as well as the latter forms[a] nearly ideal solution. Now these three mixtures (benzene with ethyl benzoate, phenetol and methyl benzoate respectively) are those which obey the volumetric rule accurately and as these are the mixtures which, from the data at hand, approach most closely to ideal solutions it may be concluded that, for ideal solutions, the simple volumetric mixture rule for dielectric constants is obeyed.

If this is so, then one should expect that the substances forming the second components of the class I(b) mixtures should show slightly higher values of internal pressure than that of benzene. By reference/

reference to table I7 this is confirmed, the values of bromobenzene, chlorobenzene, and dimethylaniline all being appreciably higher than that of benzene. The position of ethyl cinnamate is specially noteworthy; from reference to table 7 and fig.5., one sees that the dielectric constant curve of benzene - ethyl cinnamate deviates very slightly from the straight line and, in conformity with this , from table I7 the internal pressure of ethyl cinnamate is found to be only slightly greater than that of benzene and not to such a marked extent as the other members of the group. These figures, accordingly, suggest that the slight deviations from the straight line curves got for class I(b) mixtures are due to the molecules of the second components of these mixtures finding themselves in a different 'thermodynamic environment' in the mixture from that in the pure liquids, as discussed in the introduction to this section.

It may be urged that such differences of internal pressure, which are considered here, have been neglected in the discussion of the mixtures of class 2. The liquids mixed with benzene in that class, however, are all polar substances and Hildebrand lays down (loc.cit.p.I46I) that, with such substances, the changes due to chemical factors, i.e. association, are of more importance than those caused by the physical effects of internal pressure. The polarity of these molecules leads to molecular attractions and hence an internal/

internal pressure and surface tension greater than it would otherwise be. As this molecular attraction leads to association which, as we have seen, has itself an effect on the dielectric constant by causing a neutralisation of dipoles, discussion of the internal pressures for such liquids are of little value. As the internal pressures of aniline, nitrobenzene etc., are all much greater than that of benzene one should expect, in conformity with the mixtures of class I(b), that there should be a rise of dielectric constant on mixing if only changes of this nature are considered; instead there is a fall of dielectric constant showing that association changes in these cases outweigh any effects due to differences of internal pressure.

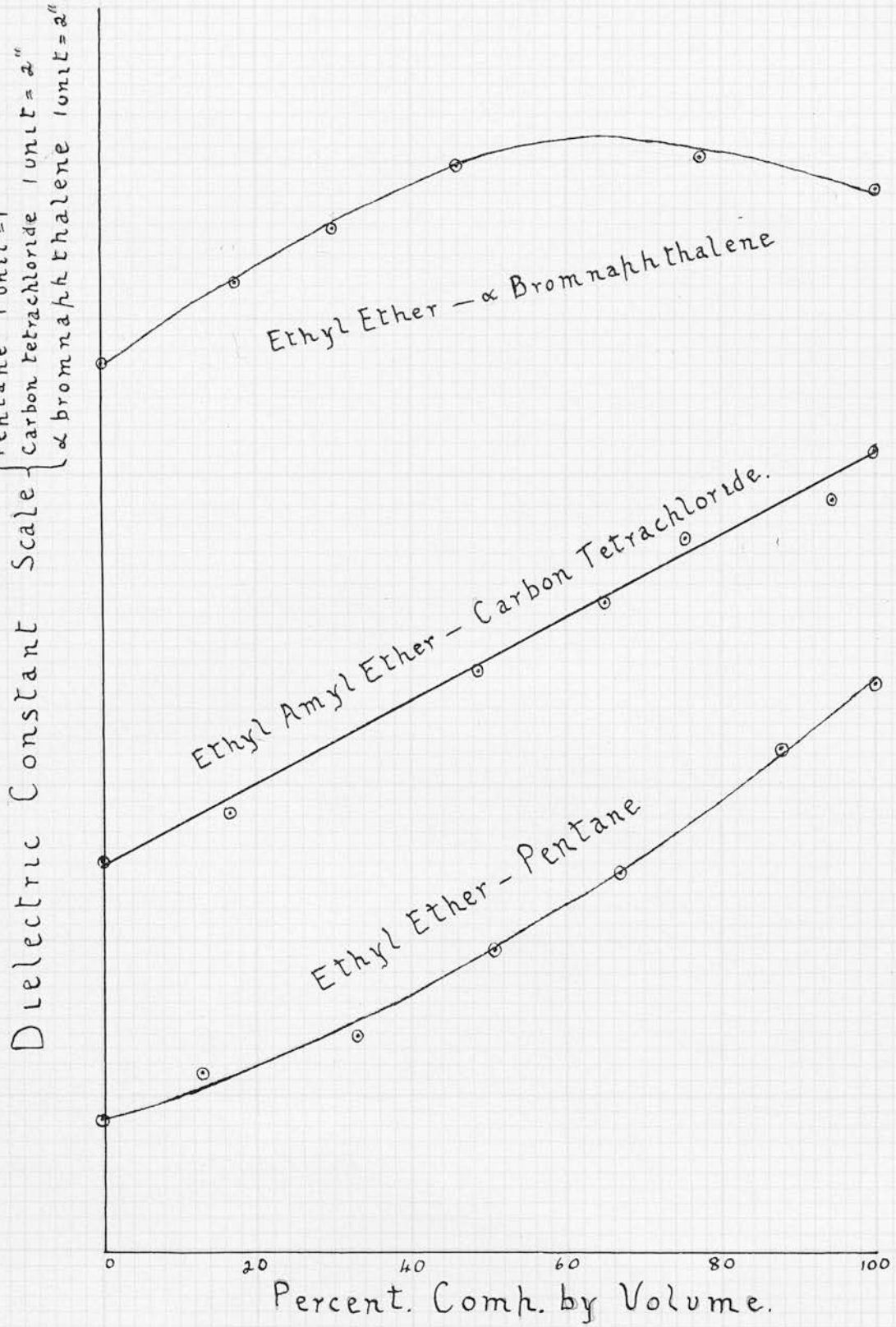
From the mixtures of classes I and 2, we may then draw the following conclusions:-

(I) for an ideal solution, the dielectric constant follows the simple volumetric rule.

(2) large deviations from this rule have been shown to be due to changes of the degree of association on mixing.

(3) slight divergence from this rule, which have been found, can be attributed to differences in the internal pressures of the components of the mixture.

Fig 11.


Dielectric Constant Scale { Pentane 1 unit = 1"
Carbon tetrachloride 1 unit = 2"
α bromnaphthalene 1 unit = 2"
Ethyl Ether — α Bromnaphthalene
Ethyl Amyl Ether — Carbon Tetrachloride.
Ethyl Ether - Pentane
0
20
40
60
80
100
Percent. Comb. by Volume.

Mixtures containing Ether as one Component.

In the mixtures for which the results have so far been given, the only cases in which there are large divergences from the mixture rule give dielectric constants much lower than required. Dobroserdoff (loc.cit.) however, described a number of mixtures which gave curves strongly concave to the axis of concentration. These mixtures all contained an ether as one component and, as they have no prototype in the benzene mixtures, it was thought of interest to enquire further into their nature.

Dobroserdoff classified his mixtures according to composition by weight; this is peculiar as from the introduction (p. 13 and see also Drude loc.cit.) the use of weight composition has no theoretical significance and, accordingly, his results were recalculated on the basis of volumetric composition; examples of the curves got in this way are given in fig. II and the classification for the ether mixtures resulted as follows:-

Class A. - straight line curves; carbon tetrachloride - ethyl amyl ether.

Class B. - curves concave to axis of concentration; mixtures of ethyl ether with chloroform, ethylene bromide and α-bromnaphthalene and those of ethyl amyl ether with chloroform and chlorobenzene.

Class C/

Class C.- curves convex to concentration axis, mixtures of ethyl ether with carbon tetrachloride, carbon disulphide, benzene and pentane.

The divergence of the curves of the last group from normal is in all cases slight and, according to the results of the first part of the investigation, two explanations are possible; it may be due either (a) to differences in the internal pressures such as have already been discussed - ether is a substance with a low pressure and accordingly, when mixed with other substances of higher pressure, the ability of the ether molecules to vibrate will be damped causing a slight fall in dielectric properties - or (b) to slight association of the ether molecules - as ether is a polar substance and all the other liquids are inert solvents, this is quite possible although ether is not generally considered to associate. The first explanation however is ruled out since the deviation is quite as pronounced with the ether-pentane mixtures as with the other mixtures; these two liquids have nearly equal internal pressures - accordingly, they should form a nearly ideal solution if there are no chemical changes and should follow the mixture rule for the dielectric constant. It would appear, therefore, that ether associates to a slight extent in these inert solvents. No explanation is forthcoming on previous considerations for the mixtures of class B and/

FIG 12.

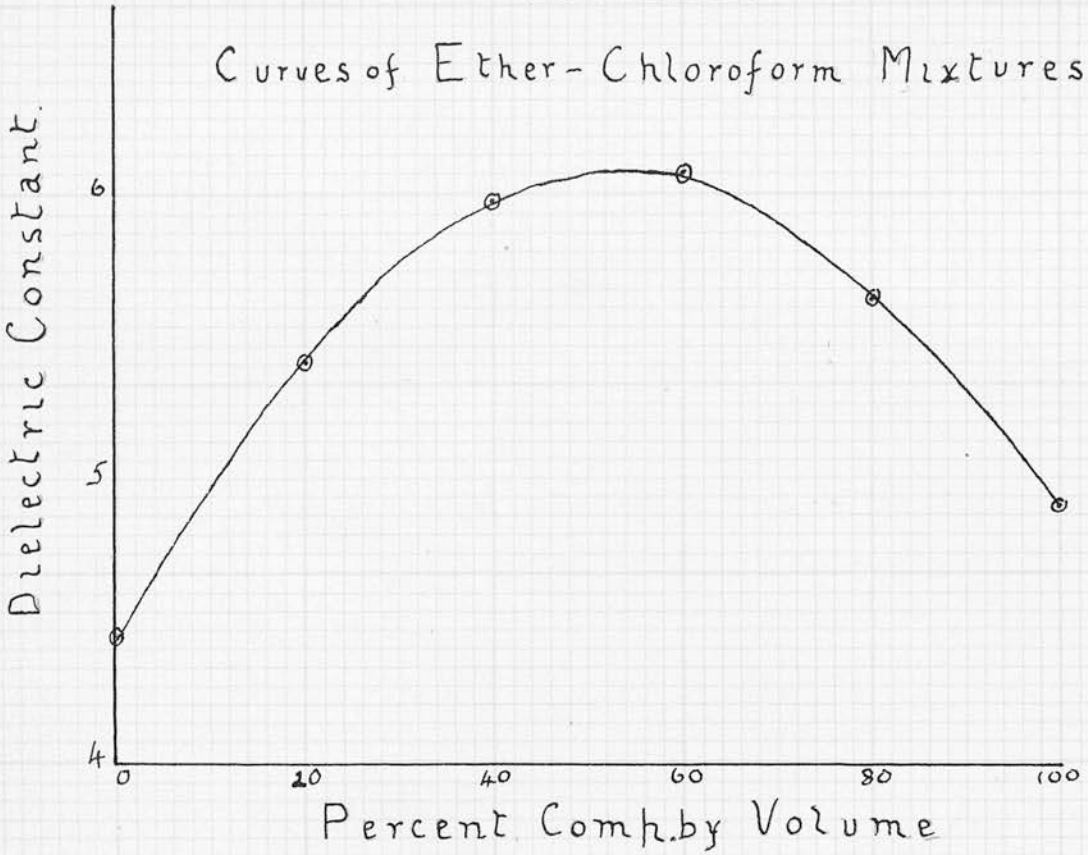
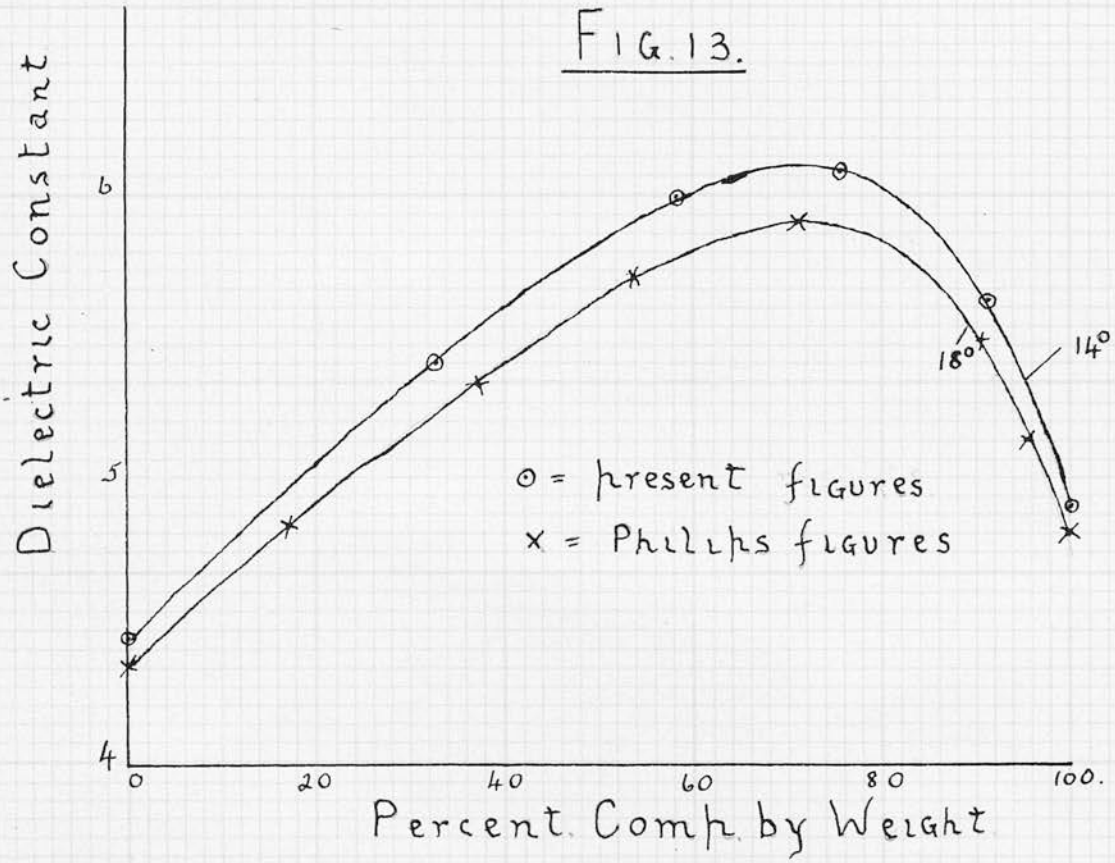

Curves of Ether-Chloroform Mixtures
Dielectric Constant.
6
5
4
0
20
40
60
80
100
Percent Comp. by Volume

FIG. 13.


Dielectric Constant
6
5
4
0
20
40
60
80
100.
18°
14°
⊙ = present figures
× = Phillips figures
Percent Comp. by Weight

and, with the object of finding others of this kind, some further mixtures were investigated.

Experimental Results.

In order to check Dobroserdoff's results, a mixture of ether-chloroform was investigated.

Table I9 Ether - Chloroform Temp. = I4.5°

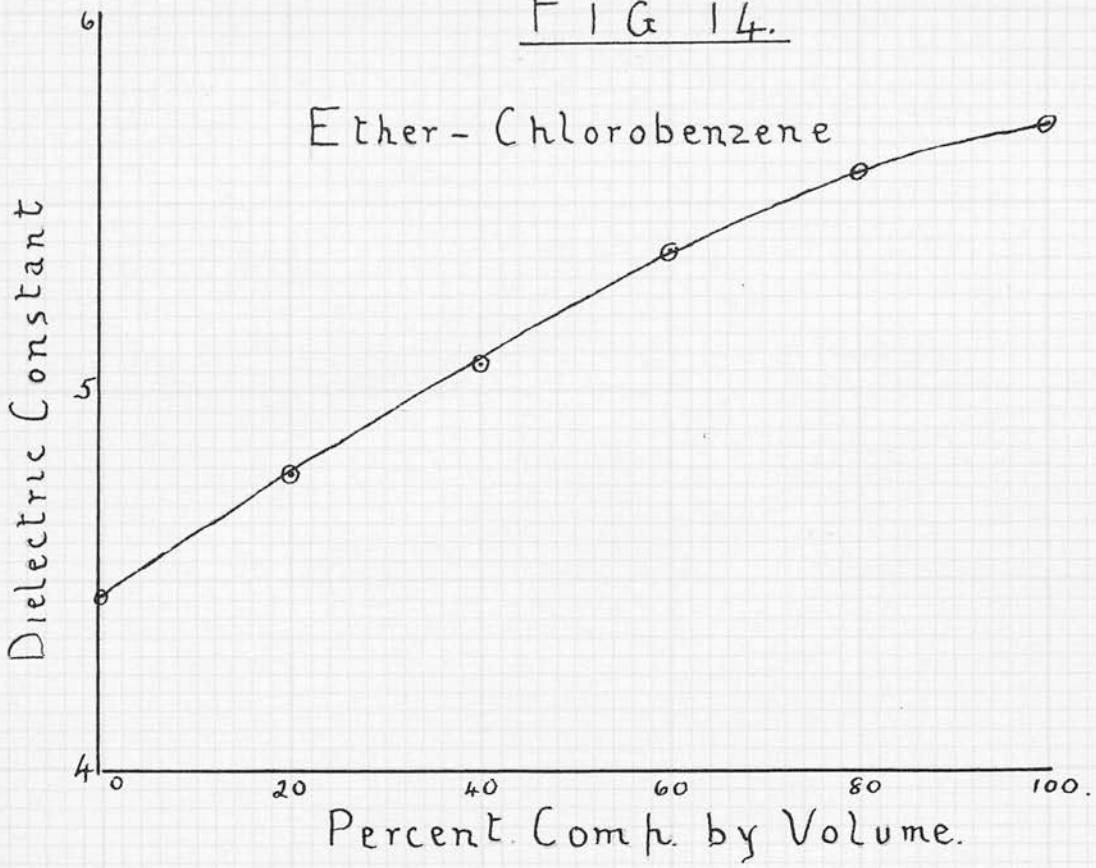
Comp.by Volume	Comp.by Weight	k.obs.	k.calc.	k.obs. - k.calc.
0	0	4.44		
20	34.4	5.4I	4.52	+ .89
40	48.2	5.99	4.62	+I.37
60	75.8	6.06	4.7I	+I.35
80	90.9	5.63	4.80	+ .83
I00	I00	4.89		

The volumetric curve is given in fig. I2 and in fig. I3, the curves of dielectric constant against weight composition obtained here and by Philip (loc.cit.) are plotted together. The latter determinations were made at a slightly higher temperature which accounts for the curve being slightly lower but otherwise the determinations agree excellently. The deviation in this case is very marked, the dielectric constant of the mixture actually rising to a value higher than that of either component.

The dielectric constants of some further mixtures containing ether as one component were now determined; the results are given in tables 20—25, and the curves of dielectric constant against composition by volume are given in figs. I4, I5, and I6.

Table/

FIG 14.


Ether - Chlorobenzene
Dielectric Constant
6
5
4
0
20
40
60
80
100.
Percent Comp. by Volume.

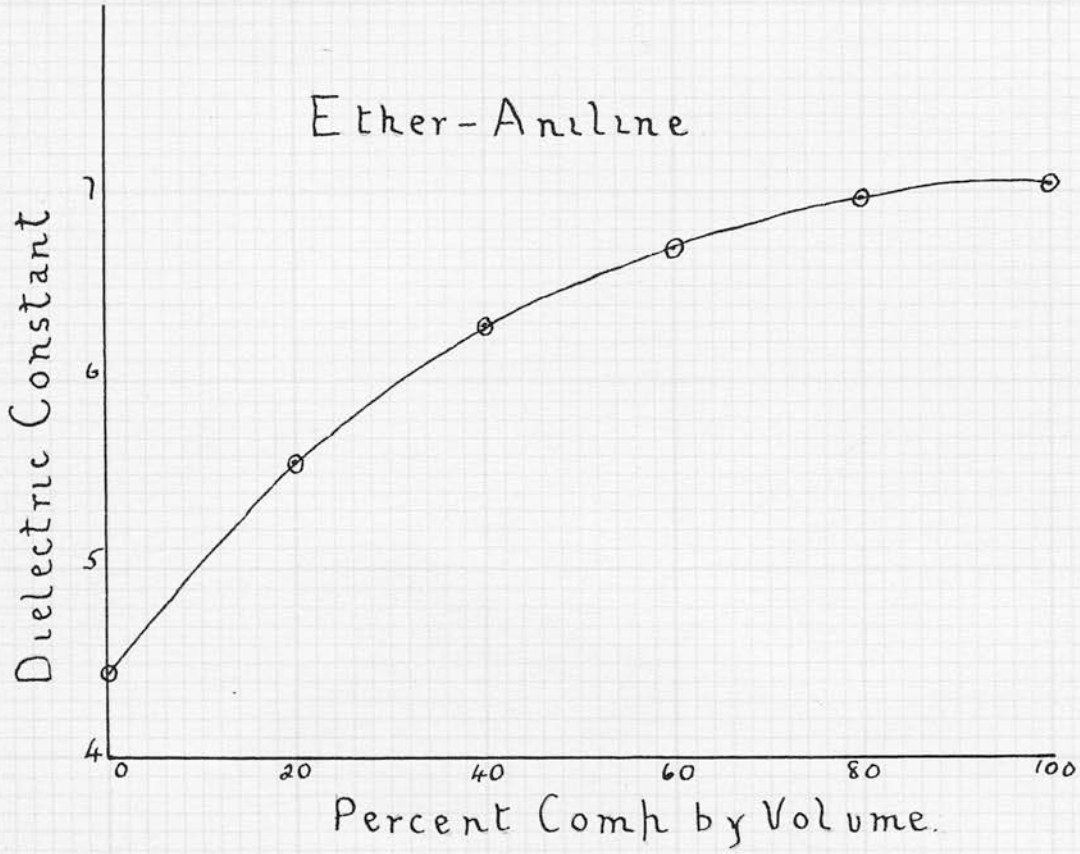

Ether - Aniline
Dielectric Constant
7
6
5
4
0
20
40
60
80
100
Percent Comp by Volume.

Table 20. Ethyl Ether - Chlorobenzene Temp. = I5°

Percent Comp. by. Volume.	Comp.by weight	k.obs.	k.calc.	k.obs. -k.calc.
0	0	4.46		
20	28.I	4.79	4.7I	+.08
40	5I.0	5.06	4.96	+.I0
60	70.6	5.37	5.20	+.I7
80	86.3	5.58	5.45	+.I3
I00	I00	5.70		

Table 2I. Ethyl Ether - Aniline Temp = I5°

Comp.by Vol.	Comp.by Wt.	k.obs.	k.calc.	k.obs. -k.calc.
0	0	4.44		
20	26.0	5.58	4.96	+.62
40	48.4	6.30	5.48	+.82
60	67.8	6.70	6.00	+.70
80	84.8	6.98	6.52	+.46
I00	I00	7.04		

FIG. 15.

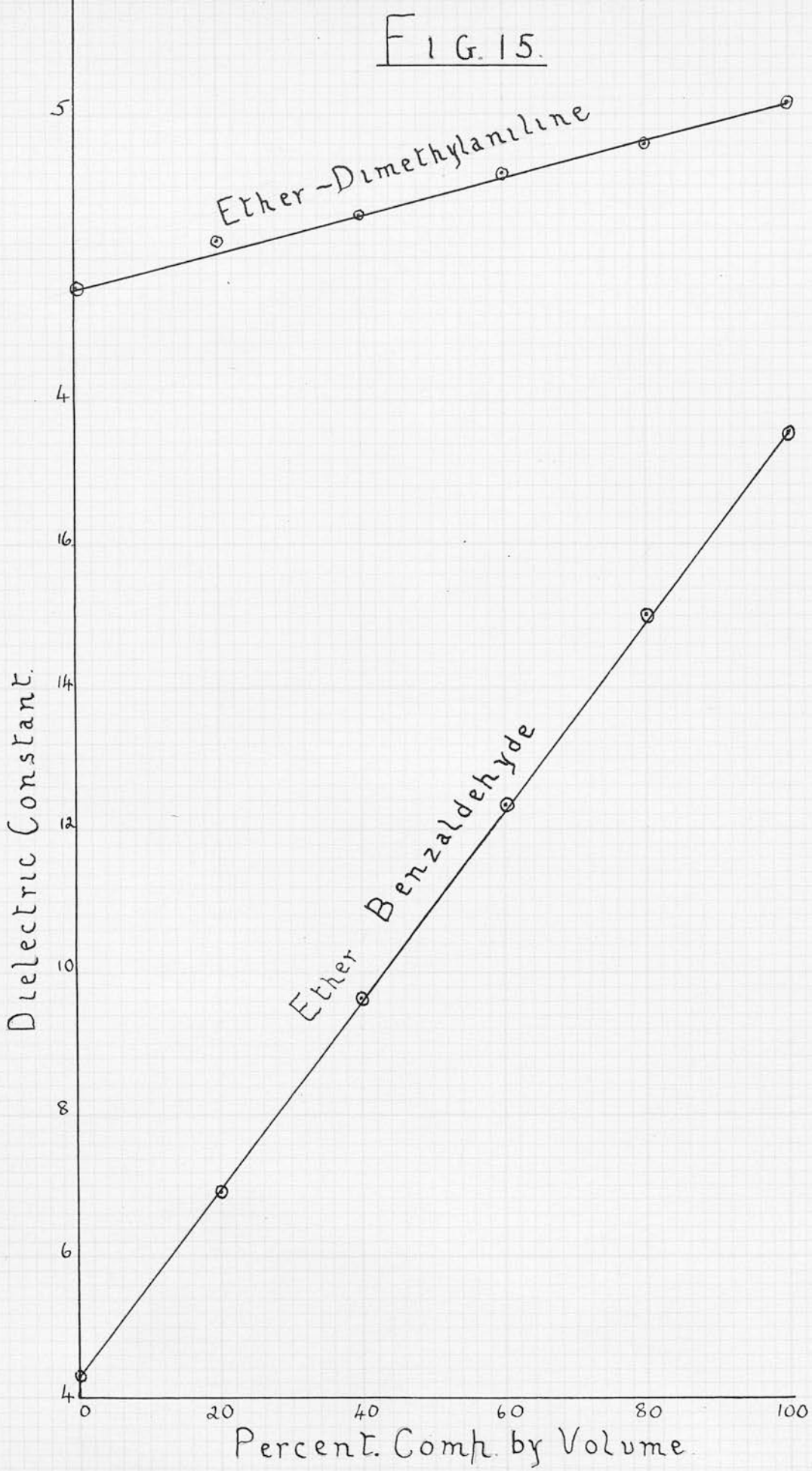

Ether - Dimethylaniline
Ether Benzaldehyde
Dielectric Constant.
5
4
16
14
12
10
8
6
4
0
20
40
60
80
100
Percent. Comp. by Volume

Table 22. Ethyl Ether - Dimethylaniline Temp = 17°

Comp.by Vol.	Comp.by Wt.	k.obs.	k.calc.	k.obs. -k.calc.
0	0	4.40		
20	24.9	4.56	4.53	+.03
40	47.1	4.65	4.66	-.01
60	66.7	4.80	4.78	+.02
80	84.3	4.90	4.91	-.01
100	100	5.04		

Table 23 Ethyl Ether - Benzaldehyde Temp = 18°

Comp.by Vol.	Comp.by Wt.	k.obs.	k.calc.	k.obs. -k.calc.
0	0	4.35		
20	26.8	6.97	7.00	-.03
40	49.3	9.65	9.65	.00
60	68.6	12.38	12.29	+.09
80	85.3	15.01	14.94	+.07
100	100	17.59		

FIG. 16.

Dielectric Constant Scale {Cresol 1 unit = 1" / Nitrobenzene 4 units = 1"
Ether - Nitrobenzene
Ether - m. Cresol
0
20
40
60
80
100
Percent Comp. by Volume

Table 24. Ethyl Ether and Nitrobenzene Temp = 20°

Comp.by Vol.	Comp.by wt.	k.obs.	k.calc.	k.obs. -k.calc.
0	0	4.35		
20	29.7	9.5I	I0.26	- .75
40	52.9	I5.07	I6.I7	-I.I0
60	7I.6	20.88	22.09	-2.2I
80	87.0	27.26	28.00	- .74
I00	I00	33.9I		

Table 25 Ethyl Ether and m-Cresol Temp = I7.5°

Comp.by Vol.	Comp.by wt.	k.obs.	k.calc.	k.obs. -k.calc.
0	0	4.4I		
20	26.4	5.94	6.I0	-.24
40	48.8	7.49	7.79	-.30
60	68.I	9.I5	9.48	-.33
80	85.0	II.00	II.I6	-.I6
I00	I00	I2.85		

Discussion of Ether Mixtures.

In the above series we are again afforded with instances of mixtures which obey the volumetric mixture rule fairly accurately; from what has been proved for the benzene series, these mixtures - ether - benzaldehyde and ether - dimethylaniline-can be accepted as normal and the behaviour of the others, deviating from this rule, must be attributed to changes on mixing. Two mixtures - ether - m.cresol and ether - nitrobenzene - give curves deviating only slightly from the straight line and have values below that required by the mixture rule. This is in good accord with what has been said regarding association in thefirst part; most polar substances, which have abnormal molecular weights in inert solvents, give, in comparison, practically normal values in ether (see Turner op.cit.) and, in conformity with this, we find cresol and nitrobenzene when mixed with ether give curves which are nearly normal; the slight deviation however shows that, although the tendency to associate is considerably lessened, association to a slight degree still takes place causing the lowering of dielectric constant observed.

The remaining mixtures - ether-aniline and ether-chlorobenzene - have curves concave to axis of concentration and belong to class B already referred to. The difference between these two mixtures and the/

and the other four cannot be attributed to internal pressure differences since all the liquids mixed with ether in these six mixtures are alike in having much higher values of the latter than ether has. It appears that some chemical explanation must be sought.

When dealing with the benzene mixtures, the only association necessary to consider was that of molecules of the same kind; this was due to one component, benzene, having a very small moment and consequently a negligible associating power. If, however, both components of the mixture be polar compounds then not only may molecules of A associate with those of their own kind but also with those of B. In such cases the sizes and the geometrical positions of the dipoles in the molecules participating in the association may be different and this would lead to the formation of various types of association products. Ebert, (Zeit.fur.Phys.Chem., 1924, 113, I), suggests that two main types are possible between which however there may be all transitional stages. Diagrams representing these types are drawn in fig.17. Reference has already been made to the first type which results in a diminution of dielectric constant. The molecules however may be considered as joining end/

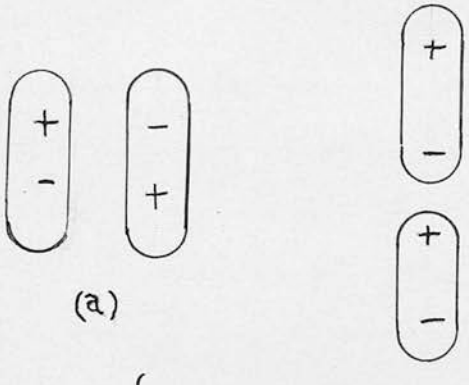


fig 17

end on to given an association of second type fig.17 (b). That this type will result in an increase of dielectric properties can be seen from reference to Debye's fundamental equation (loc.cit.). From consideration of the temperature dependence of dielectric constants he arrives at the following expression:-

$$\frac{k - I}{k + 2} \square = b + \frac{a}{T}$$

where K, d and T are the dielectric constant, density and absolute temperature respectively. The right hand side of the expression is divided into two parts; b is that caused by dielectric polarisation of the molecules i.e. due to a displacement or 'verschiebung' of the electrons from their positions of rest and a is the part due to the permanent dipoles, in the molecules. It is only with this latter part with which we are interested and for it he obtains an expression

$$a = \frac{Nm^2}{9k}$$

where N is the number of molecules per c.c. m is moment and k is Planck's universal constant. From this equation we see that a is proportional to the square of the moment. Now association of the second type causes the formation of a dipole with a moment equal to the sum of the moments of the two dipoles which have disappeared and, as the square of the moment of the single large dipole will be greater than/

than that of its two consitituents the formation of such complexes will lead to an increase of a and therefore of the dielectric constant.

The marked divergences of these mixtures under consideration cannot be explained, as already mentioned, on physical grounds; they indicate rather that changes of a more or less chemical nature are taking place. Now, as this second type of association leads to an increase of dielectric properties, it seems reasonable to suggest that these chemical changes consist of association of this kind. No definite proof could be obtained of such association from molar weight determinations by the boiling point method; such, however, can hardly be expected for the effect of this association is not to cause a diminution in the number of molecules of solute, as is the case with the previous association considered, but to cause a diminution in the number of molecules of solvent. As the solutions taken in molar weight determinations are all dilute, it will require a very much larger change to take place in the latter case than in the former to produce an appreciable change of value of molecular weight. We must fall back therefore on indirect proofs.

If the conditions governing the formation of the two types of association be considered, it is natural to expect that that of the first type (fig.17a) will take place between molecules of the same kind since in such a case the dipoles are situated in the same/

same positions in both participants of the association and, consequently, they will fit easily together. On the other hand, when the participants are molecules of different substances, there will be, in general, considerable differences in the sizes of the molecules and in the geometrical positions of the dipoles in the molecules. In consequence, the dipoles, being of different lengths, will not be able to fit together in the same way as dipoles of the same kind can, but, instead, they join end on, giving association of the second type. The condition for this type is fulfilled with these mixtures which we are considering: thus one component is ether and the other such molecules as chloroform, chlorobenzene or aniline. None of these molecules have a structure in any way similar to ether and, consequently, instead of fitting together closely as with association of the first type they join end on according to the second type. These considerations then show that, if association does take place between the components of these mixtures, one should expect it would be of the second type.

The results recorded demonstrate that, in certain cases, this association is probably actually taking place for, with the mixtures of ether with chloroform, chlorobenzene and aniline, the dielectric constants found are considerably higher than normal while those with benzaldehyde and dimethylaniline obey the mixture rule. The difference of behaviour

of/

of these compounds is interesting. Thus aniline associates with ether and yet dimethylaniline, a stronger base, does not. This shows that it is not essentially a chemical union - rather it seems to depend on the nature of the dipole. Thus in aniline the charge on one of the poles of the dipole is distributed over a smaller group than in dimethylaniline; accordingly it is more 'concentrated' and affords a better point to which the ether molecule can attach itself. Similarly with chlorobenzene and benzaldehyde, the compound with the smaller group as substitutent associates whereas that with the relatively large group, CHO, does not.

It appeared interesting to try to obtain further evidence that these different kinds of association can take place from mixtures of liquids which would be expected, from chemical evidence, to show some tendency to combine. With this in view, mixtures of aniline - m. cresol and/of acetone - chloroform (which under certain conditions form a compound) were investigated; the results are given in tables 26 and 27 and curves of dielectric constant against volumetric composition are drawn in figs. I8 and I9.

Table 26/

FIGS. 18 and 19.

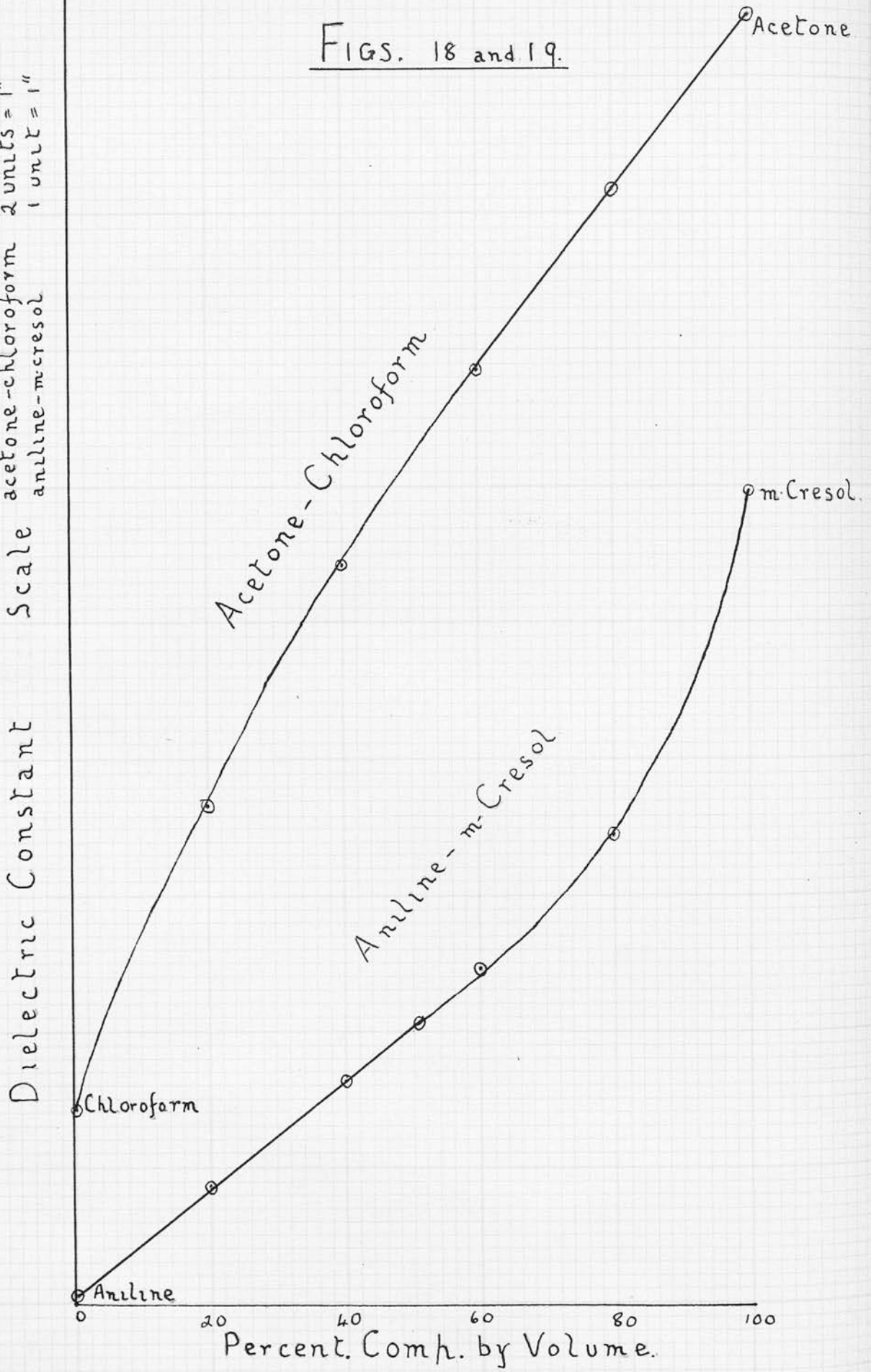


Table 26. Acetone - Chloroform Temp = I7°

Comp.by Vol.	Comp.by wt.	k.obs.	k.calc.	k.obs -k.calc.
0	0	4.85		
20	I2.5	9.37	8.06	+I.3I
40	26.I	I2.84	II.27	+I.57
60	44.3	I5.67	I4.47	+I.20
80	68.0	I8.32	I7.68	+ .64
I00	I00	20.89		

Table 27 m-Cresol - Aniline Temp = I7°

Comp.by Vol.	Comp.by wt.	k.obs.	k.calc.	k.obs. -k.calc.
0	0	7.04		
20	20.0	7.87	8.23	- .36
40	40.0	8.62	9.42	- .80
50	49.9	9.03	I0.0I	- .98
60	60.0	9.47	I0.60	-I.I3
80	80.0	I0.45	II.79	-I.34
I00	I00	I2.98		

From these figures, it is seen that the two mixtures behave in exactly opposite manners; whereas the acetone - chloroform mixture gives a curve concave to the axis of concentration, the values being greater than those required by the mixture rule, the cresol-aniline mixture gives a convex curve due to a diminution of dielectric properties on mixing. That this is in excellent agreement with what has already been said regarding the different kinds of association is evident from further consideration of the nature of the components of the mixtures. It seems, from their dielectric behaviour, that cresol and aniline associate according to the first type; this is readily understood as these two substances have molecules of approximately the same size and the dipoles will have much the same position in each. The molecules will thus be able to fit together, in the same way as moleculesof the same kind can, causing a diminution of dielectric constant. On the other hand acetone and chloroform have molecules bearing no relationship to one another in structure and the dipoles will be differently situated; the molecules associate, therefore, according to the second type and a rise in dielectric constant is got due to the formation of this type of association complex as already explained.

From the results of these ether mixtures in conjunction with the two last mixtures, it may be concluded/

concluded, then, that the influence of association on the dielectric constant depends on the type of complex formed and may lead either to an increase or decrease of dielectric constant.

Summary of Results obtained from the Dielectric Constants of Mixed Organic Liquids.

(I) For an ideal solution, the dielectric constant follows the simple volumetric mixture rule,

$$k = \frac{V_1 k_1 + V_2 k_2}{V_1 + V_2} .$$

(2) Divergences from this rule have been shown to be due to two causes: (a) physical causes whereby the molecules in the mixture behave differently from ~~those~~ in the pure state due to having a different 'thermodymanical environment' (b) chemical causes due to association taking place on mixing.

(3) Further, the results show that, while association taking place between molecules of the same kind produces a lowering of dielectric constant, another kind of association may take place between molecules of different kinds causing a rise in dielectric constant. Interesting light has been thrown on the conditions determining which of the two types of association occur.

The Dielectric Constants of Disubstituted Benzene Derivatives.

The most important use to which the dielectric constant may be applied is to determine whether a molecule has a finite electric moment or not. Molecules which have such a moment tend to set under an electric field and this setting will contribute to the dielectric properties of the molecules; hence such molecules will give an abnormally high value to the dielectric constant. It is found that, whereas benzene itself is a substance with a low value, the introduction of a substituent into the ring produces a substance which has a high dielectric constant and which departs widely from Maxwell's Law (i.e. the dielectric constant should equal the square of the refractive index) thus indicating that the molecule possesses a finite electric moment. No systematic attempt has yet been made, however, to determine what the effect of introducing another substituent into the ring is on the moment. If both substituents are of the same kind, then one should expect that the para compound, which has the most symmetrical molecule, will have the smallest and the ortho, being least symmetrical, the greatest moment, and consequently the dielectric constants should show similar variations. This view is verified for the xylenes for which data are

available/

available.

o.Xylene = 2.58 (Landolt and Jann, Zeit. fur Phys. Chem., 10, 289)

m.Xylene = 2.38 (Turner, ibid, 35, 385)

p.Xylene = 2.22 (Landolt and Jann loc.cit.)

Recently, however, J.J.Thomson (Phil.Mag. 1923, 46, 497) has made an interesting suggestion. He considers that the electrical effect of replacing an atom of hydrogen by another atom or radicle may be represented by the introduction of an electric doublet at the hydrogen atom. The sign of this doublet will depend on the nature of the substituents and he divides the radicles into two main types according to the nature of their electron configuration:-

(1) those radicles and atoms forming a system which requires an electron to forma complete octet (halogens OH., NH_2, CH_3). (2) those radicles in which there is one electron over after providing for complete octets. (NO_2, COOH, CHO, CN). The positive end of the doublet will be toward the molecule with which the radicle is combined if the substituent is of the first type, but the direction is the opposite one for the second group substituents. The electric moments of the three disubstituted benzene isomers will, in general, be different and, when this idea is applied to such derivatives, there are two possibilities. If the substituents are of the same type then the moment of the ortho should be greatest and the para least with the meta compound occupying an intermediate/

intermediate position. If, however, thetwo substituents are of different types then the effect of the two groups in the para position will not be to oppose but to reinforce one another and thus, in this case, the para will have the greatest moment and the ortho the least. This suggestion is interesting but is based on purely theoretical grounds and, with the object of testing it, an investigation of the dielectric constant of disubstituted benzene derivatives has been carried out.

Experimental Part.

In the solid state molecules are held in fixed positions by the forces of other molecules and consequently have not the freedom to set in an electric field which they possessin the liquid state: The dielectric constant of a substance in the solid state is accordingly much less than in the liquid state and it is therefore necessary to compare the dielectric constants of the three isomers all in the liquid state. (The ideal method would be to compare the dielectric constants in the gaseous state but the determinations of the dielectric constants of vapours is somewhat difficult to carry out) The choice of isomers is somewhat/

somewhat limited on this account as there are very few instances of three liquid isomers. In several cases, however, there is only one solid isomer in the three which moreover has a low melting point. It was, therefore, decided to carry out the determinations at a temperature which would allow for the inclusion as liquids of these low melting point solids. As the cell previously described could only be used easily at room temperature, it was necessary to construct a cell capable of giving results at higher temperatures i.e. which could be immersed in a thermostat. Construction of Experimental Cell. The difficulty of constructing such a cell consists in the nature of the leads from the electrodes; if a cell, such as the one already described (p.5.) be immersed in a thermostat then the leads will require to be brought out through the thermostat liquid. Now if this latter is water, the capacity between the leads is greatly increased and, what is more, subject to a marked degree to slight fluctuations of temperature owing to the high temperature coefficient of the dielectric constant of water. On the other hand, if the leads be brought out in the cell itself, they will of necessity be fairly close together and accordingly a fair capacity will exist between them, which introduces the objections mentioned in p.4. Both types of cell have been tried but the latter was found to be most suitable.

The/

The cell used in the series of determinations to be described now is represented in fig 20. The electrodes consist of two concentric cylinders made of silver and heavily gilded; the leads are fairly stout rods of similar material and are brought out as shown through a cement made of litharge and glycerine which keeps the electrodes in position and functions also as the lid of the cell. Contact to these leads is made by means of mercury cups. The cement used was found to be quite suitable being very hard and also a good insulator for high frequency currents; it was, however, attacked slightly by some hydroxylic substances. In order to test the cell, the capacity of it containing methyl benzoate was taken several times with fresh quantities of substance on each occasion. Variations at first were got but these were found to be due to differences in the quantity of liquid in the cell. Accordingly, a certain volume of liquid was taken each time and the following values were got;-

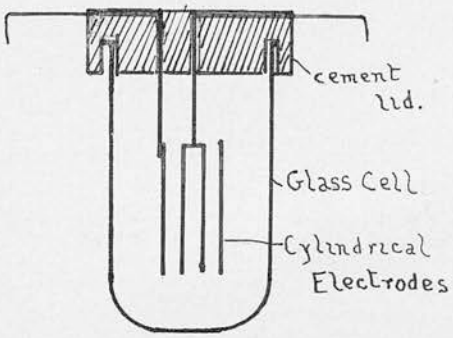


fig. 20.

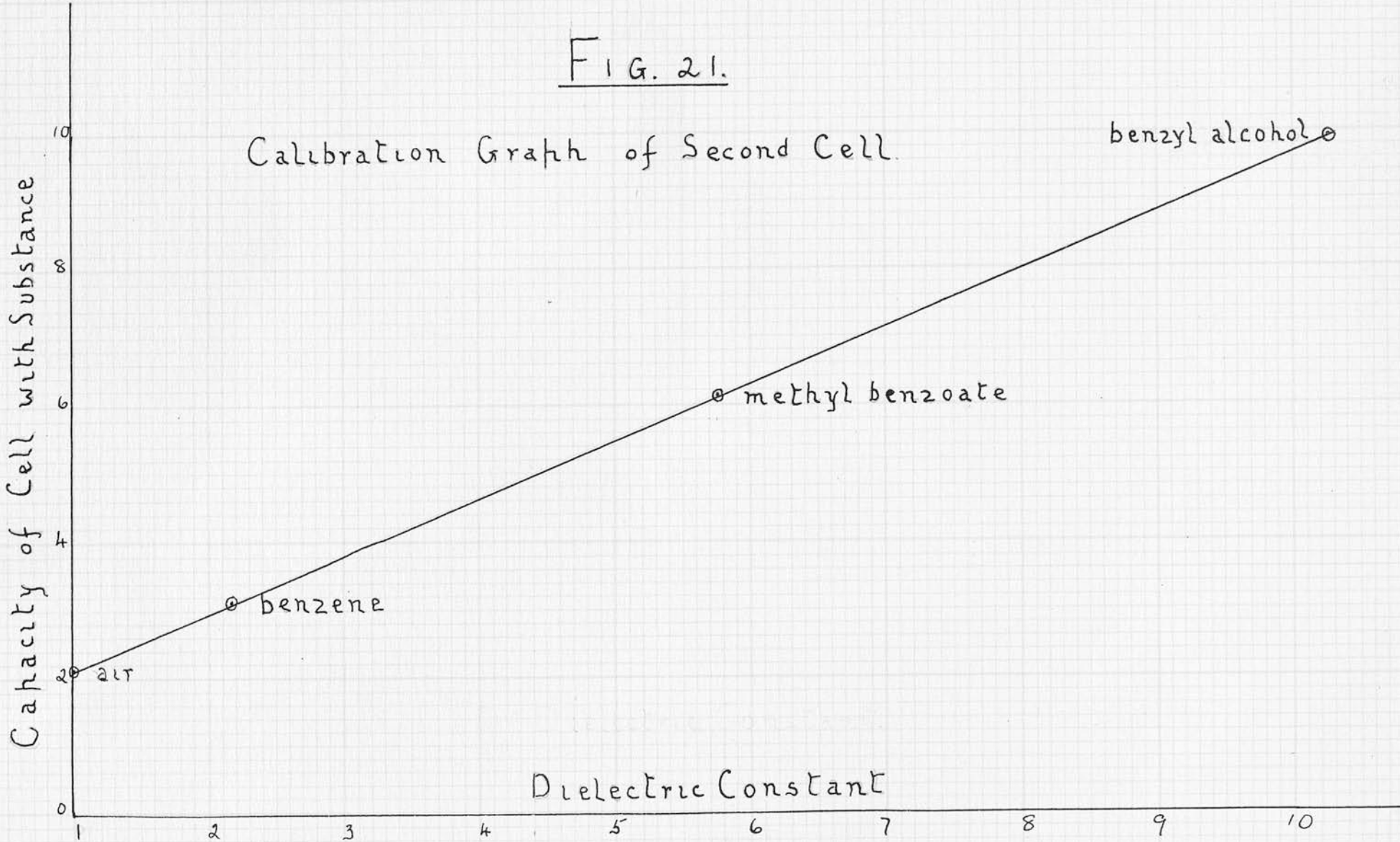
6.70, 6.70, 6.69, 6.71, 6.68, 6.69.

These figures show that the cell is capable of giving quite reproducible results; the dielectric constant however can not be obtained directly from the capacity of the cell containing the substance as there is a capacity /

capacity between the upper parts of the leads which is added each time to the capacity (proper) of the cell between the electrodes. It was, accordingly, necessary to calibrate the cell with liquids of known dielectric constant.

Method of Calibration. The dielectric constants of a number of liquids (benzene, methyl benzoate and benzyl alcohol) were obtained at the temperature, at which determinations were to be carried out (58°), by means of the cell used previously. This cell was put in a glass beaker immersed in a thermostat at the required temperature and , after two hours had been allowed for the temperature to reach equilibrium, the capacity was determined as described previously, giving the dielectric constant at that temperature. These values are subject to a slight error since the capacity of the cell with air at 58° has been taken as the same as at room temperature; the temperature coefficient of the dielectric constant of air is very small however and the only change necessary to consider will be due to expansion of the glass; for as small a range as 40° this change will be very slight and will not exert an appreciable difference in the capacity except for substances of high dielectric constant. The capacity of the new cell containing a certain volume of these liquids at the same temperature was taken and a graph was drawn on a large scale of dielectric constant against capacity of new cell/

FIG. 21.


Calibration Graph of Second Cell
Capacity of Cell with Substance
Dielectric Constant
0
2
4
6
8
10
1
2
3
4
5
6
7
8
9
10
air
benzene
methyl benzoate
benzyl alcohol

cell containing substance; a reproduction of this graph is given in fig.21. The dielectric constant could then be read directly from the graph merely by obtaining the capacity of the cell with substance. Care had to be taken throughout the determinations, to be described now, always to introduce the same amount of liquid into the cell; this was always done by pipetting the required volume (2.2 c.c. was the volume taken and as 10 c.c.were required for the other cell, this new pattern is very much more economical in material than the latter.)

Preparation of Isomers.

Some difficulty is always experienced in obtaining ortho, meta and para compounds free from one another owing to the marked resemblances which their physical properties have. The method used herein consisted of purifying the toluidines and where possible obtaining the compounds desired from them by means of the diazo reaction.

o.Toluidine was purified by means of a method described by Lewy (Ber.,1886,19,1717). The phosphate of o.toluidine is readily soluble in cold water whereas that of p.toluidine is almost insoluble; also when o.toluidine phosphate is treated with p-toluidine or aniline, the o.toluidine is liberated as free base and the other base forms a salt. Advantage was taken of/

of these facts to purify o.toluidine by means of treating it with syrupy phosphoric acid, adding water and allowing to stand overnight. The o.toluidine, after separation and drying, was found to boil fairly constant, B.P. I92.2° - I92.8° M.P. acetyl derivative =III°. Before determining the dielectric constant this liquid was fractionally distilled and a nearly colourless liquid was obtained, b.p. 200.7 (press. 758mm.

m.Toluidine. No suitable method is given in the literature for the purification of m.toluidine but a practical method was obtained for m.nitrotoluene. The method (Reissert, Ber., I897, 30, I030) consists of condensing m.nitrotoluene with sodium ethoxide and diethyl oxalate. The ortho and para nitrotoluenes react thus $NO_2C_6H_4.CH_3 + C_2H_5O.CO.COOC_2H_5 \longrightarrow C_2H_5OH + NO_2C_6H_4CH_2CO.COO\ C_2H_5$ (nitrophenylpyruvic acid) whereas the meta compound does not react at all. On condensation taking place the liquid turns a deep red colour due to the sodium salt of the above acid; to ensure that the reaction was going properly a condensation was carried through using B.D.H. m.nitrotoluene and half molecular quantities of the other reagents, a very deep red colouration was got; the product so obtained was again condensed using half molecular quantities, but this time only a faint red colour was obtained, indicating that practically all the ortho and para compounds/

compounds had been removed. m.Nitrotoluene after being treated in this way was recovered and reduced to m.toluidine by means of iron and acetic acid; the compound so obtained was used for diazotisation. b.p. 202.5° - 203° m.p. acetyl derivative = 67°. For the dielectric constant determinations the liquid was still further purified by distillation until a nearly colourless liquid was got, b.p. 203° - 203.2° ((press. = 755 mm.).

p.Toluidine. This isomer is easily purified by means of crystallisation which was carried out twice from aqueous alcohol. Beautiful white crystals were obtained, m.p. = 43.5°, m.p. acetyl derivative = I49°. Before the dielectric constant was determined the p.toluidine was freshly distilled b.p. = 200.5° (press. = 75I mm.).

Chlorotoluenes. The three chlorotoluenes were prepared from the respective toluidines by means of Sandmeyer reactions; in each case the compounds were fractionated until a constant boiling fraction was obtained.

ortho.	b.p. =	I58.8° - I59°
meta.	b.p. =	I6I.2° (press. = 736 mm.)
para	b.p. =	I6I.2° - I6I.4° (press. = 744 mm.)

Bromotoluenes. The three bromotoluenes were obtained by the same method as for the chloro-

toluenes/

toluenes.

ortho b.p. = 179.2° - 179-4° (press. = 738 mm.).

meta b.p. = 183.5° - 183.8° (press = 760 mm.).

para m.p. = 24.5°

Nitrotoluenes. Ortho. No suitable chemical method amongst those given in the literature could be obtained for the separation of small amounts of para from o-nitrotoluene (cf. van der Arend Rec.Trav.Pays. Bas,1909,28 410). The commercial product, however, is purified by freezing out the para compound and a sample obtained from B.D.H. was found to boil only slightly above the value given in the literature (the boiling point of the para compound is much higher i.e. 238°). This product was fractionated three times until a fairly constant boiling fraction was obtained, b.p. 221.5° - 222° (press. = 747 mm.) To make sure it was quite dry, the liquid, before use, was distilled under reduced pressure over P_2O_5, both the meta and para compounds being treated in the same way.

Meta-nitrotoluene. was purified as already described and fractionated several times until a constant boiling fraction was obtained, b.p. = 231.5° - 232°.

Para. The B.D.H. product after recrystallization from absolute alcohol was found to melt quite sharply at 51.5°. The value generally quoted in the literature, 54°, appears to be erroneous for Rintoul (J./

(J.Soc.Chem.Ind. 1915,34,60) after several crystalizations obtained a value of 51.6° - 51.9° and Halleman (Rec.Trav.Pays Bas. 1914,33,5) quite independently found a value of 51.4°. The value found here is in excellent agreement with these values and the B.D.H. substance recrystallized from absolute alcohol and distilled under reduced pressure over P_2O_5 was used.

Cresols. Ortho and Para. The B.D.H. products of both these isomers were distilled under reduced pressure over P_2O_5 ; both liquids solidified readily on seeding but neither gave sharp melting points, ortho, m.p. = 29.7° para, m.p.=33.2° As the boiling points of each were quite sharp this lack of sharpness in the melting point was probably due to the solids absorbing moisture on being introduced into the melting point tube as both are very hygroscopic. In order to make sure that the substances used were quite dry, immediately before use they were distilled over P_2O_5 under reduced pressure.

ortho b.p. = 75.5° (press. = 10 mm.).

para b.p. = 87.5° (press = 10 mm.).

Meta. m.cresol was obtained from m.toluidine by means of the diazo reaction. It was distilled twice under reduced pressure and then finally over P_2O_5. The sample was still slightly yellow coloured but the boiling point was constant.

b.p. = 87.5° (press = 10 mm.)

Dichlorobenzenes/

Dichlorobenzenes Ortho and Para. The B.D.H. products of ortho and para dichlorobenzene were employed; both were redistilled and constant boiling fractions were obtained in each case. The para compound was found to melt quite sharply at the value quoted in the literature. Before use both were distilled over P_2O_5 .

ortho b.p. = 177.5° - 178° (press.=750 mm.)
= 58° (press - 10 mm.)
para b.p. = 173.5° (press =750 mm.)
m.p. = 53°

The Meta compound was prepared from m.chloraniline by means of a Sandmeyer reaction and after several fractionations a constant boiling fraction was obtained, which, before use, was likewise distilled under reduced pressure over P_2O_5 .

b.p. = 172° - 172.2° (press = 752 mm.)
= 55.5° (press. = 10 mm.)

Chlorophenols Ortho and para chlorophenols were obtained from B.D.H. and were treated in the same way as the dichlorobenzenes.

ortho b.p. = 175.3° - 175.5° (press=750 mm.)
para b.p. = 217.5° - 218° (press=750 mm.)

Dielectric Constant Determinations.

The dielectric constant of the above substances have all been determined at $58^{\circ} \pm .2^{\circ}$ and the results are given in table 28; each value was checked by the repetition, if necessary more than once, of the determination with a fresh quantity of substance. The values for the monosubstituents have also been determined, the substances in each case being carefully purified and, for comparison, the results are also given in this table. As there are slight differences in density between the different isomers which will cause a different number of molecules to be present in unit volume of each, density determinations were carried out at 58° by means of a pyknometer and the results are given in the first column. The values of the dielectric constant occupy the second column, in the third there is given the quantity $\frac{k \times M}{d}$ i.e. the dielectric constant estimated for the same number of molecules as advocated by J. J. Thomson (loc.cit.), and in the last column, the quantity $\frac{k - I}{k + 2} \frac{M}{d}$, the molecular polarisation according to Ebert (loc.cit.) which will be discussed later. The values of the various quantities for benzene, toluene and the xylenes were obtained from Landolt Bornstein Tabellen and are added in table 29.

Table 28/

Table 28. Values of the Dielectric constant.

Temp. = 58° Wave length = 95 metres.

Substance	D_4^{58}	Dielectric Constant(k)	$\frac{k \times M}{d}$	$\frac{k-1}{k+2} \cdot \frac{M}{d}$
Chlorobenzene	I.064	5.23	553	6I.8
o.Dichlorobenzene	I.256	7.00	838	78.0
m.Dichlorobenzene	I.244	4.63	548	64.7
p.Dichlorobenzene	I.248	2.62	308	29.8
Aniline	.9887	6.20	538	59.7
o.Toluidine	.9665	5.7I	633	67.7
m.Toluidine	.9586	5.45	609	66.7
p.Toluidine	.9542	4.88	548	63.3
Nitrobenzene	I.I65	28.00	2958	95.I
o.Nitrotoluene	I.I26	2I.6I	263I	I06.3
m.Nitrotoluene	I.I2I	2I.86	2673	I06.9
p.Nitrotoluene	I.II7	22.22	2728	I07.5
Chlorobenzene	I.064	5.23	553	6I.8
o.Chlorotoluene	I.044	4.I6	504	62.I
m.Chlorotoluene	I.035	5.04	6I6	70.I
p.Chlorotoluene	I.03I	5.55	68I	73.9
Bromobenzene	I.444	4.92	535	6I.2
o.Bromotoluene	I.344	4.28	544	66.4
m.Bromotoluene	I.309	5.36	700	77.4
p.Bromotoluene	I.3I4	5.49	7I4	78.0
Phenol	I.075	9.90	866	65.I
o.Cresol	I.0I2	6.02	643	66.9
m.Cresol	I.0I3	9.68	I033	79.3
p.Cresol	I.004	9.9I	I064	80.5
o.Chlorophenol	I.2I8	5.4I	57I	62.5
p.Chlorophenol	I.247	9.46	975	76.0

Table 29 Data of Other Investigators.

Temp. = 20° Wave length = ∞

Substance	D_4^{20}	k	$\frac{k \times M}{d}$	$\frac{k-1}{k+2} \cdot \frac{M}{d}$
Benzene	.8786	2.28	202	26.6
Toluene	.8659	2.33	248	32.7
o'Xylene	.8633	2.58	3I7	42.4
m.Xylene	.8620	2.38	293	38.7
p.Xylene	.86II	2.22	273	35.7

Discussion of Results.

According to Thomson's theory, which it was the object of this investigation to test, of the radicles contained in the above compounds, CH_3, Cl, Br, NH_2 and OH all belong to the first type of radicles and NO_2 to the second. Accordingly all these compounds, with the exception of the nitrotoluenes, have both substituents belonging to the same type and therefore the dielectric constants estimated for the same number of molecules should be in order o > m > p. It was found, however, that only the dichlorobenzenes and the toluidines give this order. The dielectric constants of the nitrotoluenes are in the order o < m < p but, as in this case the substituents are of different types, this order is in agreement with that required by Thomson. The more detailed discussion of the various isomers will now be divided into two parts, the isomers which agree with Thomson's theory being discussed first and those not in agreement second.

Only three of the sets of isomers investigated follow this theory, - the dichlorobenzenes, toluidines and nitrotoluenes. The agreement of the dichlorobenzenes is most striking. Thomson considers the case especially where both substituents are of the same kind. Neglecting the deflection of the two doublets/

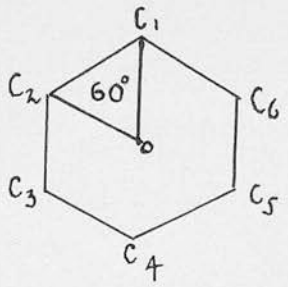


fig. 22.

doublets due to their action on each other, he arrives at the following expressions making use of fig. 22. (where I is the moment of the doublet for one substituent)

(1) If the two substituents are in the para position to one another, the resultant moment is zero.

(2) If they are in positions ortho to one another then the resultant moment is $(\mathcal{J}^2 + \mathcal{J}^2 + 2\mathcal{J}^2 \cos 60°)^{\frac{1}{2}} = \sqrt{3}.\mathcal{J}$.

(3) If they are in the meta positions then the resultant moment is $(\mathcal{J}^2 + \mathcal{J}^2 + 2\mathcal{J}^2 \cos 120°)^{\frac{1}{2}} = \mathcal{J}$

That is to say, the para substituent destroys the moment and should make the molecule non polar, the meta compound has a moment nearly equal in magnitude to the monosubstituted compound and the ortho has a larger moment . These predictions are in excellent agreement with the experimental values for the dichlorobenzenes. The ortho compound has a dielectric constant higher than chlorobenzene but the value of the meta compound estimated for the same number of molecules (column 3.) differs only slightly from that of chlorobenzene and the value of the para compound is only slightly greater than that for benzene. Analogous results are obtained for the xylenes (table 29), the para compound in this case again having the smallest value and the ortho greatest but/

but the agreement is better when the moments, calculated by the methods to be mentioned shortly, are taken. The following values are given for the moment in a summary included in Henri's 'Structure des Molécules'.

	$\mu \times 10^{19}$		$\mu \times 10^{19}$
Benzene =	2	o.Xylene =	5.8
Toluene =	4.9	m.Xylene =	4.6
		p.Xylene =	2.3

Thus the moments of the meta and para compounds are approximately equal to those of toluene and benzene respectively, in accord with the results obtained with the dichlorobenzenes and with Thomson's theory; The toluidines are also in agreement with this theory; NH_2 and CH_3 are both groups belonging to the same type and moreover bear a certain resemblance to one another in structure; the moments of the compounds should therefore be in the order o > m > p and this is the order which their dielectric constants are found to be in. The nitrotoluenes, which are the other isomers obeying Thomson's theory, have their dielectric constants in the reverse order from the isomers already considered. As toluene is a substance with a very small moment, the doublet representing the introduction of a methyl group must be small and thus the difference of effect due to its various positions should not be great. This is found to be the case with the nitrotoluenes, the three isomers not showing much difference in their dielectric constants. The order with the para greatest is explained quite simply on Thomson's suggestion that the/

the doublet representing the CH_3 group is of a different kind from that for the NO_2 group and thus the two doublets oppose one another in the ortho position and reinforce in the para.

Turning now to the compounds which do not obey Thomson's theory, these are the chlorotoluenes, the bromotoluenes, the cresols, and the chlorophenols. In all cases the dielectric constant of the ortho should be greatest and the para least but, actually, it is found that the order is reversed and the ortho compounds have very much lower values than the para. It has already been mentioned that the CH_3 group introduced into the benzene ring causes only a slight moment. Instead of the CH_3 group exerting a very small effect in the different positions as one would expect and as is the case for the nitrotoluenes, it is found however that the introduction of the methyl group in chlorobenzene, bromobenzene and phenol causes markedly different effects according to its position, the ortho compounds in all cases having the smallest dielectric constant and the para greatest. These three sets of isomers then depart widely from Thomson's theory. Even if it be assumed that this divergence is due to an error in the division of the radicles and that CH_3 on the one hand, and Cl, Br, OH on the other should really be classed as different types, one should still expect the chlorophenols to follow/

follow the order suggested but here again it is found that the ortho has a smaller moment than the para instead of a larger. It may be quite definitely concluded from these results, then, that Thomson's theory in itself is not sufficient to explain the behaviour of the dielectric constants of the disubstituted benzene derivatives. Two conclusions may however be drawn from the figures obtained (I) the three isomers show a regular gradation of their dielectric constants from ortho to para (2) in certain cases there is an increase and in others a decrease of dielectric constant in passing from ortho to para.

Up till now, in accord with the method of Thomson, the dielectric constant simply estimated for the same number of molecules has been taken as a measure of the electric moment. The actual theoretical relationship between the moment and the dielectric constant has been derived by Debye whose equation and expression for the moment havebeen given on p 45. Although his theory holds fairly satisfactory for gases it breaks down when applied to liquids as it fails to take adequate account of the orienting influence of the molecules upon one another. Gans (Ann.d.Phys., I92I, 64, 48I) has developed a more general equation which has the form:-

$$\frac{k-I}{k+2}\cdot\frac{I}{d} = C + \frac{A}{T}\cdot\phi\left(\frac{T\sqrt{1-\gamma d}}{B\sqrt{d}}\right)$$

where C can be calculated from optical data, A,B and γ are/

are constants which depend on the electric moment and other molecular constants and ϕ is a function introduced by Gans in his theory of paramagnetism. This formula has been modified into a simpler form by Smyth (Phil.Mag. 1923,45,849) and, by means of it, he has calculated the moments of a large number of molecules (J.Amer.Chem.Soc. 1924,46.2151). In the above equation it is not the dielectric constant itself which is taken to calculate the moment but the function, $\frac{k-1}{k+2} \cdot \frac{1}{d}$, and it seems accordingly more feasible to compare this expression for various substances. This quantity however is a measure of the moment produced per gram and to be really comparable molecular quantities should be taken; the values of $\frac{k-1}{k+2} \cdot \frac{M}{d}$, have therefore been calculated and are given in the last column of table 28. The use of this expression has been advocated by Ebert (loc.cit.) who terms it the molecular polarisation. The values of this expression for the various isomers have the same order as the dielectric constants but the position of the monosubstituent relative to the disubstituents is changed when this function is used. Thus nitrotoluene has a dielectric constant estimated for the same number of molecules (column 3) higher than the nitrotoluenes but the molecular polarisation is smaller (column 4.) Since the dielectric constants and consequently the moments of the three nitrotoluenes do not differ by much, it is probable,

from/

from analogy with benzene and toluene, that the moment of nitrobenzene will also have nearly the same value. The molecular polarisation of that compound, however, is found to be smaller than that of the nitrotoluenes. It does not follow from this, nevertheless, that the moment is also lower since no account has been taken of the quantities entering into the right hand side of Gans' equation which are a measure of the differing molecular fields. Now the molecular volume of nitrobenzene is different from those of the nitrotoluenes, which are all nearly equal, and it is quite probable therefore that the molecular field in the former is different from those prevailing in the latter liquids. Comparisons of the moments of the mono- and di- substituents cannot therefore be carried out, with any degree of certainty, merely from the respective dielectric constants; this is unfortunate as such comparisons are necessary before any conclusions can be drawn regarding the effect of introducing substituents in different positions but, before such can be done, determinations of the actual moments must be carried out. Although there must be certain differences due to the varying electric moments of the isomers, it may be assumed that the molecular fields of the three isomers are of much the same nature since the molecular volumes and consequently the distances between the molecules therein are nearly equal. Accordingly the changes in molecular polarisation/

polarisation for the three isomers may be taken as indicating actual changes in the value of the electric moment.

The number of isomers examined and also the lack of experimental data of other kinds do not permit of any general conclusions being drawn here as to what are the influences causing the ortho compound to have the greatest moment in some cases but the least in others. Thus no simple explanation can be got for the moments of the chlorotoluenes and those of the toluidines being in different orders. There is an essential difference, however, between the compounds which obey Thomson's theory and those which do not - with the former the fall of dielectric constant from ortho to meta is approximately equal to that from meta to para but with the latter the difference between meta and para is much less than that between ortho and meta. It appears therefore that the CH_3 group in the ortho position in the latter compounds exerts a stabilising effect on the molecule and tends to prevent the polarisation of the molecule as a whole by the other radicle. This action by the CH_3 group is possibly due to ~~te~~ some induced effect on it brought about by neighbouring radicle when the latter is Cl, Br or OH but which is not exerted by the NH_2 radicle. Such an explanation, however, in no way accounts for the behaviour of the chlorophenols. Thus there seems no apparent reason why p.chlorophenol should have a moment quite comparable with each of the monosubstituents/

monosubstituents when p.dichlorobenzene has only a very small moment. The explanation of the behaviour of the chlorophenols will only be possible when other disubstituted compounds have been investigated in which both radicles as monosubstituents give large moments.

SUMMARY.

(I) The dielectric constants of a number of disubstituted benzene derivatives in the liquid state have been determined.

(2) The three isomers show in all cases a regular gradation of their dielectric constants from ortho to para.

(3) In some cases there is an increase and in others a decrease in passing from ortho to para.

(4) Where both substituents are the same the order is o > m > p.

(5) A theory, proposed by Sir J.J.Thomson, predicting what substituents would bring about the two different gradations of dielectric constants has been tested but, although agreement has been obtained in some cases, this theory has not been able to account for the behaviour of all the isomers.

(6) Divergences, it is suggested, may be due to mutual induced effects of the substituents on one another.